

7

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) Publication number : **0 562 819 A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number : **93302193.3**

(51) Int. Cl.⁵ : **G03F 7/004**

(22) Date of filing : **23.03.93**

(30) Priority : **23.03.92 JP 94956/92**

(43) Date of publication of application :
29.09.93 Bulletin 93/39

(84) Designated Contracting States :
DE FR GB IT NL

(71) Applicant : **JAPAN SYNTHETIC RUBBER CO., LTD.**
11-24, Tsukiji-2-chome Chuo-ku
Tokyo 104 (JP)

(72) Inventor : **Murata, Makoto**
9-10-701, Cyuubu
Tokkaichi-shi, Mie-ken (JP)
Inventor : **Ota, Toshiyuki**
57-1-4, 3654-banchi, Uneme-cho
Yokkaichi-shi, Mie-ken (JP)
Inventor : **Yumoto, Yoshiji**
3698-1, Uneme-cho
Yokkaichi-shi, Mie-ken (JP)
Inventor : **Miura, Takao**
22-6, Mitakidai 2-chome
Yokkaichi-shi, Mie-ken (JP)

(74) Representative : **Clifford, Frederick Alan et al**
MARKS & CLERK 57/60 Lincoln's Inn Fields
London WC2A 3LS (GB)

(54) **Resist coating composition.**

(57) There is provided a resist coating composition which contains a radiation-sensitive acid-forming agent selected from the group consisting of an onium salt compound, a halogen-containing compound, a sulfone compound, a nitrobenzyl compound and a sulfonate compound and at least one solvent selected from methyl 3-methoxypropionate and ethyl 3-ethoxypropionate. The resist coating composition has an excellent storage stability, which is capable of giving excellent resist sensitivity and an excellent form of a pattern with good reproducibility even after storage of a prepared resist solution for a long period of time.

EP 0 562 819 A2

Detailed Description of the Invention

The present invention relates to a resist coating composition. More specifically, it relates to a resist coating composition suitable for ultrafine processing by means of radiation such as i-ray or far ultraviolet light.

5 In the field of fine processing typified by the production of integrated circuits, the processing size in lithography is becoming finer, and in recent years, there is required a technology by which a fine processing for a breadth of 0.5 μm or less can be stably performed. Therefore, a resist used for this purpose is required to form a pattern having a line breadth of 0.5 μm or less with good accuracy. Therefore, studies on lithography using radiation having a shorter wavelength (300 nm or less) are under way.

10 The above radiation includes ultraviolet light typified by i-ray (365 nm), far ultraviolet light typified by KrF excimer laser (248 nm), X-ray typified by synchrotron radiation and charged corpuscular beam typified by electron beam. A variety of resists for use with these radiations have been proposed recent years.

Among these resists, attention is particularly being brought to resists which undergo a reaction to change their solubility in a developer solution by the catalytic activity of an acid formed when exposed to radiation.

15 These resists are generally called "chemically amplified resists".

When a resist is actually used in a process for producing integrated circuits, generally, a resist solution (to be referred to as "resist coating composition" hereinafter) is prepared by dissolving resist components such as a radiation-sensitive component, a coating-forming component, etc., in a solvent, and spin-coated or roll-coated on a substrate to be processed, thereby to form a resist coating. Therefore, the performances of the resist coating composition such as coatability and storage stability are essential for stably carrying out highly fine processing. Further, the resist coating forms a pattern suitable for fine processing when exposed to radiation, and the form of the pattern has a crucial influence on the accuracy of fine processing. Generally, a rectangular solid form is considered to be desirable.

20 European Patent Publication No. 0 211 667A2 discloses a radiation-sensitive resin composition comprising a solution of an alkali-soluble resin and a radiation-sensitive compound in a solvent which comprises a monooxymonocarboxylic acid ester.

The above European Patent Publication describes that when the above composition is positive, 1,2-quinonediazide compound is used as the radiation-sensitive compound, and that when it is negative, an azide compound is used as the radiation-sensitive compound. The above European Patent Publication also discloses 3-methoxypropionic acid methyl ester as the monooxymonocarboxylic acid ester.

30 Japanese Laid-open Patent Publication No. 98,652/1988 discloses a positive radiation-sensitive composition containing (A) an alkali-soluble resin, (B) at least one member selected from polyolefinsulfone and halogenated polyolefin sulfone and (C) a solvent containing monooxymonocarboxylic acid ester. This composition is not a chemically amplified composition. This Japanese Laid-open Patent Publication discloses methyl 3-methoxypropionate as the monooxymonocarboxylic acid ester (C).

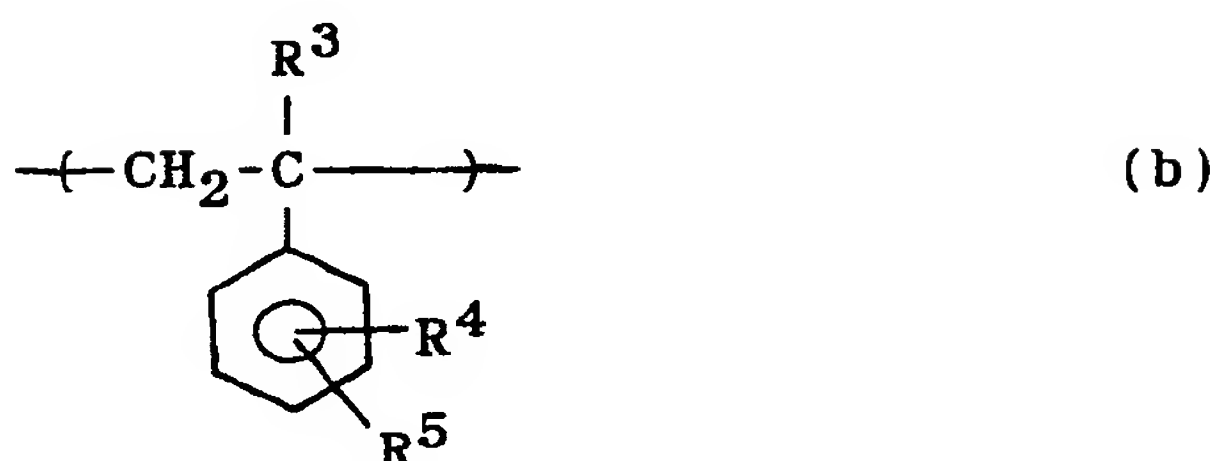
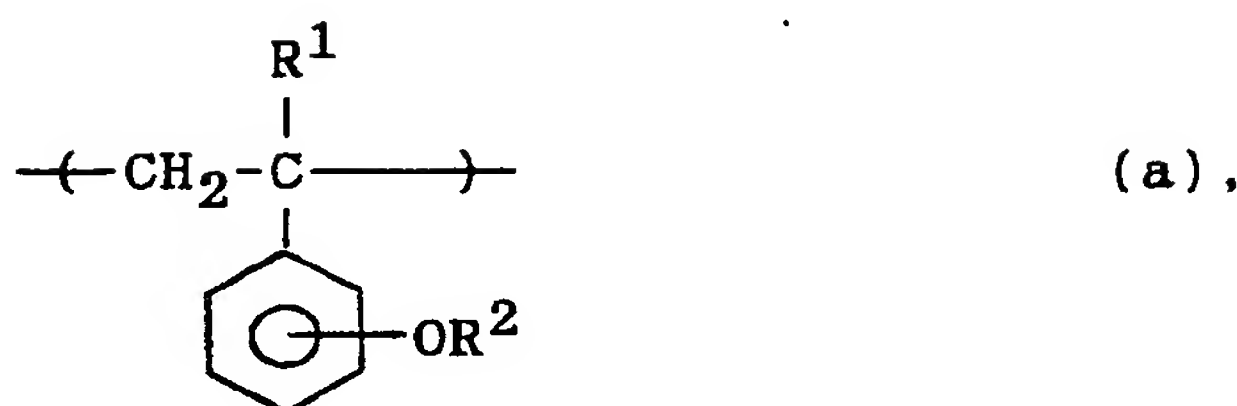
Japanese Laid-open Patent Publication No. 107,161/1991 discloses a resist composition containing (A) an alkali-soluble phenolic resin and (B) a 1,2-naphthoquinonediazide-4-sulfonic acid ester of a compound having a phenolic hydroxyl group as a sensitizer. This Japanese Laid-open Patent Publication also discloses that the above resist composition may additionally contain (C) a compound which is acid-cleavable under irradiation of actinic radiation, such as an onium salt, a halogenated organic compound and a halogenated organic compound/organic metal mixture. Further, this Japanese Laid-open Patent Publication describes that the solvent used for applying the above resist composition to a substrate is selected from methyl 2-oxypropionate, ethyl 2-oxypropionate, methyl 2-methoxypropionate and ethyl 2-methoxypropionate.

45 Japanese Laid-open Patent Publication No. 107,160/1991 discloses a resist composition containing (A) an alkali-soluble hydrogenated phenolic resin, (B) a compound which can be acid-cleavable under irradiation with actinic radiation and (C) a dissolution inhibitor having an acid-decomposable group.

The above Japanese Laid-open Patent Publication discloses that the above compound (B) and the solvent can be selected from the same compounds as those described in the previous Japanese Laid-open Patent Publication No. 107,161/1991. Further, it is disclosed that specific examples of the dissolution inhibitor include compounds having an Si-O-C bond, compounds having an Si-N bond and compounds having a C-S-C bond.

50 The above Japanese Laid-open Patent Publication No. 101,760/1991 describes, as mentioned above, that the invention intends to provide a resist composition well-balanced among Sensitivity, resolution, etching resistance and storage stability by using not a phenolic resin but a hydrogenated phenolic resin.

Japanese Laid-open Patent Publication No 107,165/1991 discloses a resist composition containing a copolymer having structural units of the formulae (a) and (b) in the molecular chain,



wherein each of R^1 and R^3 is H or an alkyl group, R^2 is an alkyl group, $-\text{SO}_2\text{R}^6$ or $-\text{CO}_2\text{R}^6$, in which R^6 is an alkyl group or an aryl group, and each of R^4 and R^5 is H, a halogen atom or an alkyl group, and a compound acid-cleavable under irradiation with actinic radiation.

The above resist composition has a characteristic feature in the use of the above copolymer which is sparingly soluble in an alkali and is modified to become soluble in an alkali when exposed to light.

Japanese Laid-open Patent Publication No. 107,163/1991 a resist composition containing an alkali-soluble phenolic resin, a compound which is acid-cleavable under irradiation with actinic radiation and spiro-orthocarbonate.

The characteristic feature of the above resist composition is that it contains the above spiro-orthocarbonate which has the property of inhibiting the dissolution of the alkali-soluble phenolic resin in a developer solution and the property of promoting the dissolution of the alkali-soluble resin in the developer solution in the presence of an acid derived from an agent which generates an acid with irradiation of light.

European Patent Publication No. 0 419 147A2 discloses a resist composition comprising:

- (A) a hydrogenated alkali-soluble phenolic resin,
- (B) a compound capable of generating an acid on irradiation; and
- (C) a compound capable of crosslinking in the presence of the acid.

The above European Patent Publication describes that the above compound (B) and the solvent are selected from those described in the previous Japanese Laid-open Patent Publication No. 107,161/1991. It is also described that the above compound (C) includes compounds having a group of $-\text{C}-\text{O}-\text{alkyl}$ and compounds having an epoxy group.

Japanese Laid-open Patent Publication No. 107,164/1991 discloses a resist composition containing (A) a photosensitive resin prepared by modifying an alkali-soluble phenolic resin with a photosensitive compound and (B) a compound which is acid-cleavable under irradiation with actinic radiation. It discloses that the photosensitive compound to modify the alkali-soluble phenolic resin includes diazidesulfonic acid ester, a diazo-carbonyl compound and an o-nitrobenzyl compound. It is described that the above compound (B) and the solvent are selected from those described in the previous Japanese Laid-open Patent Publication No. 107,161/1991.

Japanese Laid-open Patent Publication No. 328,747/1992 discloses a photoresist composition comprising a polymer resin, a photosensitive compound and an ethyl-3-ethoxypropionate solvent. Example 3 of this Japanese Laid-open Patent Publication describes that a preparation of trifluorosulfonyloxybicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide (MDT) in a polyhydroxystyrene-poly-t-butoxycarbonyloxystyrene copolymer was treated with propylene glycol methyl ether acetate and ethyl 3-ethoxypropionate, and the coating formed by spin-casting was measured for its film uniformity of the silicon wafer.

U.S. Patent 4,965,167 discloses a light-sensitive composition useful as a positive-working photoresist, comprising an admixture of:

- (a) at least one alkali-soluble binder resin, preferably a phenolic novolak resin;
- (b) at least one photoactive compound, preferably a photoactive o-quinonediazide compound, and
- (c) a sufficient amount of a solvent mixture comprising ethylacetate and 3-ethoxy propionate to dissolve (a) and (b).

U.S. Patent 4,943,511 discloses a positive photosensitive composition containing a solvent which is selected from the group consisting of (1) a mixture of ethyl Cellosolve acetate, butyl acetate and xylene; (2) a mixture of propylene glycol monomethyl ether acetate, butyl acetate and xylene; (3) ethyl-3-ethoxy propionate; (4) propylene glycol monomethyl ether acetate; and (5) a mixture of propylene glycol monomethyl ether acetate, butyl acetate and ethyl 3-ethoxy propionate.

The above positive photosensitive composition contains also a photosensitizer which is a mixture of mono-, di- and tri-esters of 2,3,4-trihydroxybenzophenone and 1,2-naphthoquinone-2-diazo-4-sulfonyl chloride and a novolak resin.

European Patent Publication No. 0 273 026A2 discloses a composition comprising a single-phase liquid mixture of: (a) at least one photoactive component (PAC) consisting of an oxo-diazonaphthalene sulfonate or carboxylate polyester of a polyhydroxy ballast compound; (b) at least one alkali soluble phenolic resin; and (c) a solvent.

It is disclosed that the specific examples of the solvent include methyl-3-methoxypropionate and ethyl-3-methoxypropionate.

As is disclosed in some of the above prior art documents, it is known, that a resist containing a novolak resin and a naphthoquinonediazide-containing sensitizer, used in conventional lithography using visible light or ultraviolet light, can achieve the above-described performances by using an ethyl cellosolve- or methyl cellosolve-containing compound as a solvent used for the preparation of a resist coating composition. Concerning "chemically amplified resist", a resist coating composition has a problem in storage stability when ethyl 2-oxypropionate is used as a solvent for preparing the resist coating composition.

That is, a chemically amplified resist containing ethyl 2-oxypropionate as a solvent has a problem in that the sensitivity of the resist and the form of a pattern vary with the passage of time after a resist solution has been prepared.

It is an object of the present invention to provide a novel resist coating composition.

It is another object of the present invention to provide a resist coating composition suitable as a resist composition which permits stable fine processing, has an excellent storage stability and gives an excellent form of a pattern.

It is further another object of the present invention to provide a resist coating composition having an excellent storage stability, which is capable of giving excellent resist sensitivity and an excellent form of a pattern with good reproducibility even after storage of a prepared resist solution for a long period of time.

Other objects and advantages of the present invention will be apparent from the following description.

According to the present invention, the above objects and advantages of the present invention are achieved, first, by a positive resist coating composition (to be referred to as "first resist coating composition" hereinafter) comprising:

- (a) an alkali-soluble resin (to be referred to as "resin (A)" hereinafter),
- (b) at least one radiation-sensitive acid-forming agent selected from the group consisting of an onium salt compound, a halogen-containing compound, a sulfone compound, a nitrobenzyl compound and a sulfonate compound,
- (c) a compound (to be referred to as "solubility controller" hereinafter) which has the property of controlling the alkali solubility of the (a) alkali-soluble resin and which is decomposed in the presence of an acid to develop either the property of reducing or losing the effect of controlling the alkali solubility of the (a) alkali-soluble resin or the property of promoting the alkali solubility of the (a) alkali-soluble resin, and
- (d) at least one solvent selected from methyl 3-methoxypropionate (to be referred to as "MMP" hereinafter) and ethyl 3-ethoxypropionate (to be referred to as "EEP" hereinafter).

Further, according to the present invention, the above objects and advantages of the present invention are achieved, second, by a positive resist coating composition (to be referred to as "second resist coating composition" hereinafter) comprising:

(ac) a resin (to be referred to as "resin (B)" hereinafter) which has at least one acid-decomposing group selected from a substituted methyl group, a 1-substituted ethyl group, a silyl group, a germyl group, an alkoxycarbonyl group and an acyl group and is insoluble or sparingly soluble in an alkali, and which is alkali-soluble when the above group is acid-decomposed,

(b) at least one radiation-sensitive acid-forming agent selected from the group consisting of an onium salt compound, a halogen-containing compound, a sulfonate compound, a nitrobenzyl compound and a sulfone compound, and

(d) at least one solvent selected from methyl 3-methoxypropionate (MMP) and ethyl 3-ethoxypropionate (EEP).

Furthermore, the above objects and advantages of the present invention are achieved, third, by a negative resist coating composition (to be referred to as "third resist coating composition" hereinafter) comprising:

(a) an alkali-soluble resin (resin (A)),

(b) at least one radiation-sensitive acid-forming agent selected from the group consisting of an onium salt compound, a halogen-containing compound, a sulfonate compound, a nitrobenzyl compound and a sulfone compound,

5 (c') a compound (to be referred to as "crosslinking agent" hereinafter) which crosslinks the (a) alkali-soluble resin in the presence of an acid, and

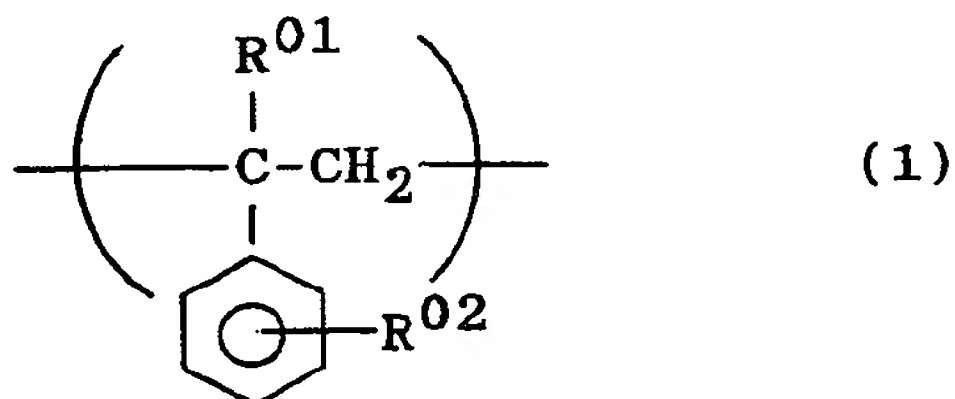
(d) at least one solvent selected from methyl 3-methoxypropionate (MMP) and ethyl 3-ethoxypropionate (EEP).

10 The above resist coating compositions of the present invention will be explained hereinafter. Each component of the resist coating compositions will be explained first.

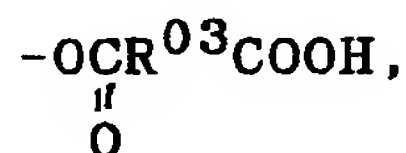
Resin (A)

15 The resin (A) used in the first and third resist coating compositions is not specially limited if it has the property of being soluble in an alkali developer solution.

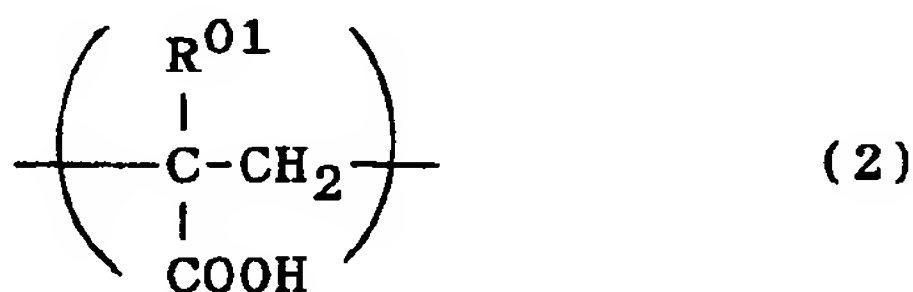
Therefore, the resin (A) is only required to be a resin having a functional group having affinity to an alkali developer solution, e.g., an acidic functional group such as a phenolic hydroxyl group or a carboxyl group. As the resin (A), preferred is a polymer having at least one recurring unit selected from the group consisting of a recurring unit of the formula (1),



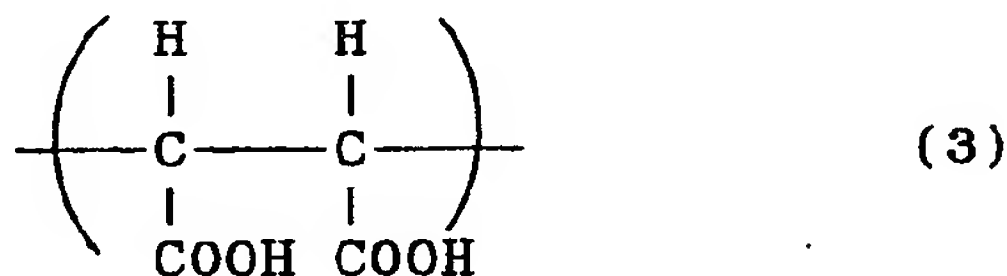
20 wherein R⁰¹ is hydrogen atom or a methyl group, R⁰² is a hydroxyl group, a carboxyl group, a group of -R⁰³COOH, a group of -OR⁰³COOH or a group of



35 in which R⁰³ is an alkylene group having 1 to 4 carbon atoms, a recurring unit of the formula (2),

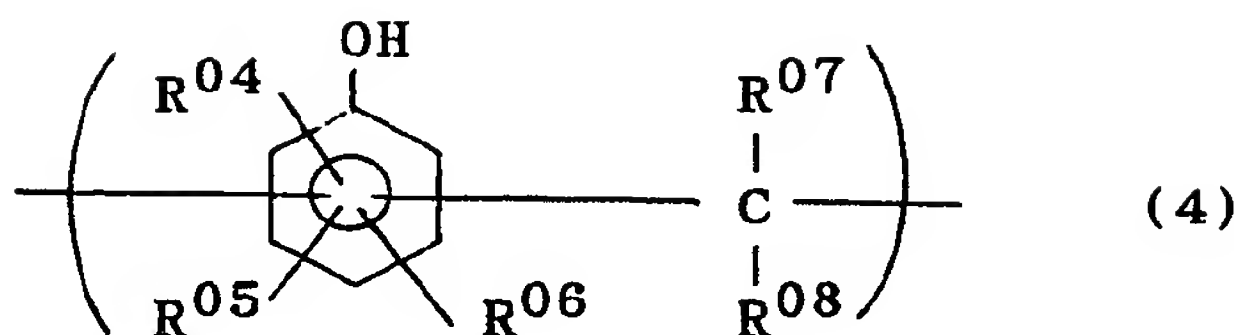


45 wherein R⁰¹ is as defined in the above formula (1), a recurring unit of the formula (3),



50 and a recurring unit of the formula (4),

55



wherein each of R⁰⁴, R⁰⁵, R⁰⁶, R⁰⁷ and R⁰⁸ is independently hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

The resin (A) may be composed of recurring units of any one of the formulae (1), (2), (3) and (4) alone. It may also contain other recurring unit. The "other recurring unit" includes recurring units derived from the cleavage of double bonds of monomers having a double bond such as styrene, methyl styrene, alkyl (meth)acrylate containing an alkyl group having 1 to 4 carbon atoms, maleic anhydride, fumaronitrile, acrylamide, acrylonitrile, vinylpyridine, vinylpyrrolidone, vinylimidazole and vinylaniline when a polymer contains recurring units represented by the formulae (1), (2) or (3).

Although not uniformly determined due to the content of other recurring unit, the content of the recurring units of the formulae (1), (2), (3) and (4) is generally at least 15 mol%, preferably at least 20 mol%.

The molecular weight (to be referred to as "Mw" hereinafter), i.e., weight average molecular weight as a polystyrene measured by gel permeation chromatography (to be referred to as "GPC"), of the resin (A) is preferably 1,000 to 150,000, particularly preferably 3,000 to 100,000.

The resin (A) used in the present invention can be obtained by polymerizing a corresponding vinyl monomer or by polycondensing a phenol or phenol derivative and an aldehyde or an aldehyde derivative.

The resin (A) that contains the recurring unit of the formula (1) or (2) can be also used in the form of a hydrogenation product having a hydrogenation ratio of 70 % or less, preferably 50 % or less, more preferably 40 % or less.

Resin (B)

As the resin (B) used in the second resist coating composition, preferred is a resin which is obtained by replacing hydrogen atom of the acidic functional group, i.e., phenolic hydroxyl group or carboxyl group, of the above resin (A) with at least one acid-decomposing group (to be referred to as "substituent B" hereinafter) selected from a substituted methyl group, a 1-substituted ethyl group, a silyl group, a germyl group, an alkoxy-carbonyl group and an acyl group and which is insoluble or sparingly soluble in an alkali. The term "acid-decomposing group" refers to a group which can be decomposed in the presence of an acid.

Specific examples of the substituent B include a substituted methyl group such as methoxy methyl, methylthiomethyl, methoxyethoxymethyl, tetrahydropyranyl, tetrahydrofuranyl, tetrahydrothiopyranyl, tetrahydrothiofuranyl, benzyloxymethyl, phenacyl, bromophenacyl, methoxyphenacyl, α -methylphenacyl, cyclopropylmethyl, cyclohexyl, cyclopentyl, benzyl, triphenylmethyl, diphenylmethyl, bromobenzyl, nitrobenzyl, methoxybenzyl and piperonyl; a 1-substituted ethyl group such as 1-methoxyethyl, 1-ethoxyethyl, isopropyl, t-butyl and 1,1-dimethylpropyl; a silyl group such as trimethylsilyl, triethylsilyl, t-butyldimethylsilyl, isopropyl dimethylsilyl and diphenyldimethylsilyl; a germyl group such as trimethylgermyl, triethylgermyl, t-butyldimethylgermyl, isopropyl dimethylgermyl and phenyldimethylgermyl; an alkoxy carbonyl group such as methoxycarbonyl, ethoxycarbonyl and t-butoxycarbonyl; and an acyl group such as acetyl, propionyl, butyryl, heptanoyl, hexanoyl, valeryl, pivaloyl, isovaleryl, lauryloyl, myristoyl, palmitoyl, stearoyl, oxalyl, malonyl, succinyl, glutaryl, adipoyl, piperoyl, suberoyl, azelaoyl, sebacoyl, acryloyl, propioloyl, methacryloyl, crotonoyl, oleoyl, maleoyl, fumaroyl, mesaconoyl, camphoroyl, benzoyl, phthaloyl, isophthaloyl, terephthaloyl, naphthoyl, toluoyl, hydro-atropoyl, atropoyl, cinnamoyl, furoyl, thenoyl, nicotinoyl, isonicotinoyl, p-toluenesulfonyl and mesyl.

Of the above substituents, preferred are t-butyl, benzyl, tetrahydrofuranyl, tetrahydropyranyl, tetrahydrothiofuranyl, tetrahydrothiopyranyl and t-butoxycarbonyl.

The substituent B is introduced, for example, through the acid functional group of the resin (A). The amount of the introduced substituent B based on the total amount of the acidic functional group of the resin (A) is preferably 15 to 100 %, more preferably 20 to 80 %. The molecular weight, Mw, measured by GPC, of the resin (B) is preferably 1,000 to 150,000, particularly preferably 3,000 to 100,000.

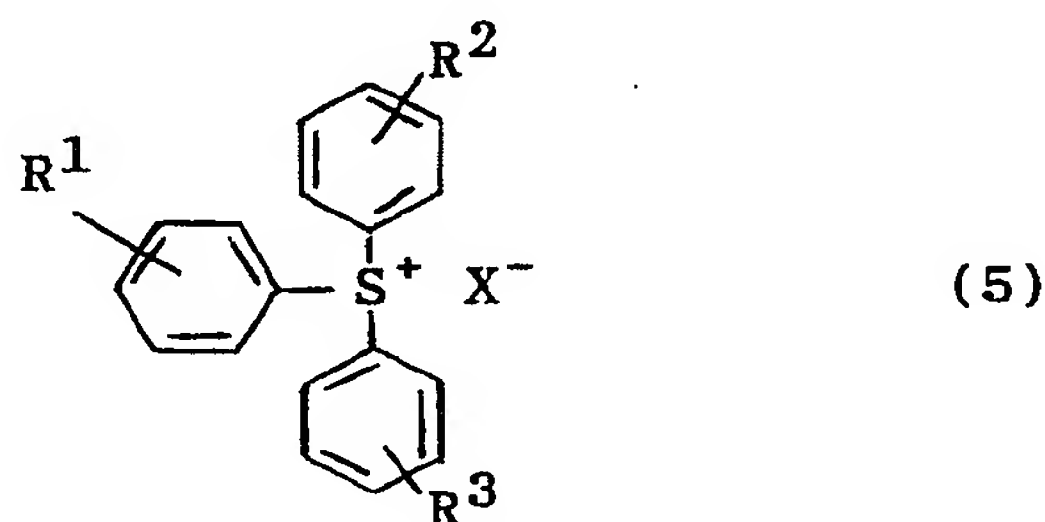
The resin (B) is insoluble or sparingly soluble in an alkali. The term "sparingly soluble in an alkali" refers to the following property of the resin (B). That is, when a coating formed of the resin (B) alone instead of the resist coating is developed with an alkali under the alkali-development conditions suitable for forming a pattern on a resist coating formed of the second resist coating composition, the resin (B) remains in such a coating

thickness that is at least 50 % of the initial coating thickness of the resin (B) after the above development procedure has finished.

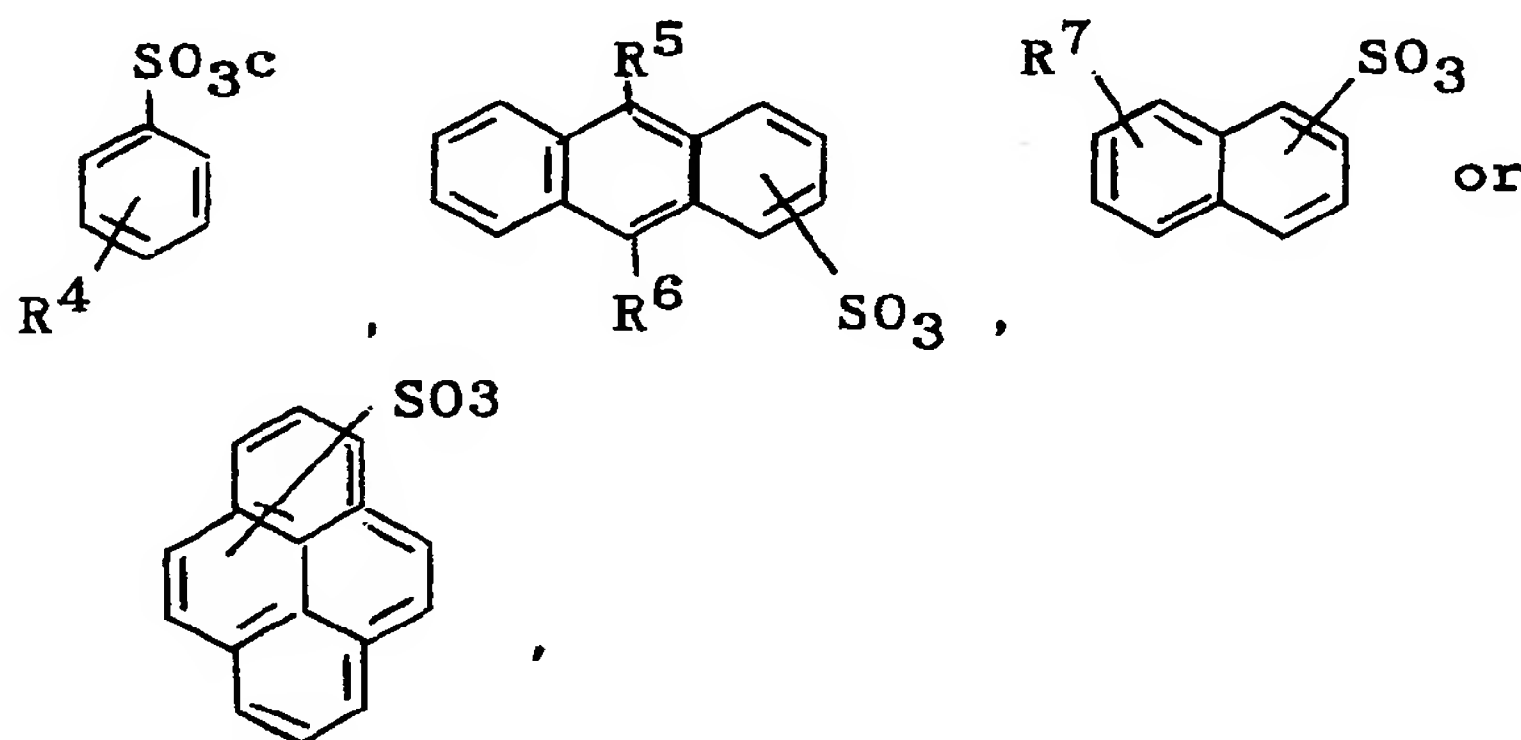
Radiation-sensitive acid-forming agent

The radiation-sensitive acid-forming agent, i.e., a compound which generates an acid by responding to radiation, used in the present invention, includes an onium salt compound, a halogen-containing compound, a sulfone compound, a sulfonate compound and a nitrobenzyl compound. Specific examples thereof are as follows.

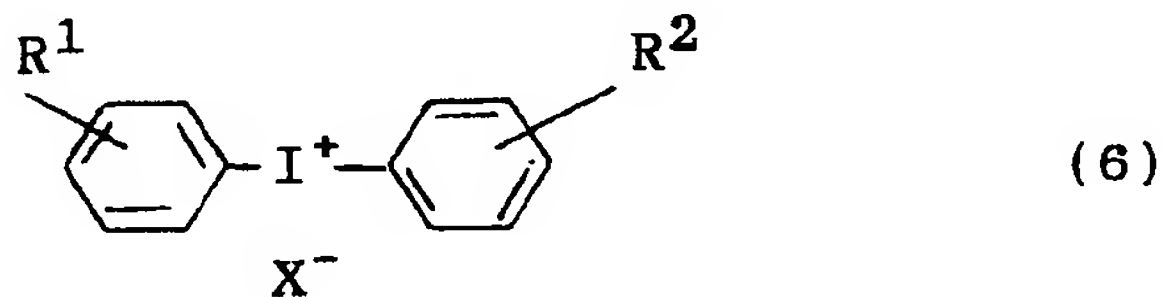
Examples of the onium salt include iodonium salt, sulfonium salt, phosphonium salt, diazonium salt and pyridinium salt. Preferred is at least one onium salt selected from the group consisting of sulfonium salt of the formula (5),



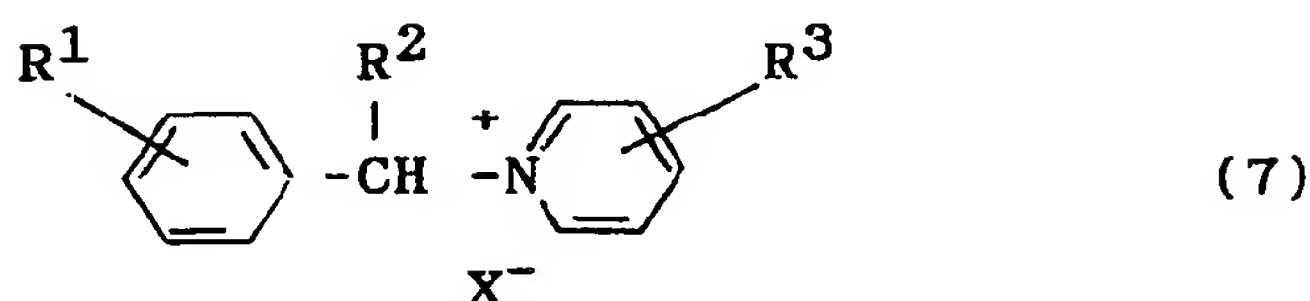
wherein each of R¹, R² and R³ is independently hydrogen atom, a hydroxyl group, an amino group, a nitro group, a cyano group, an alkyl group having 1 to 4 carbon atoms or an alkoxy group having 1 to 4 carbon atoms, and X is SbF₆, AsF₆, PF₆, BF₄, CF₃CO₂, ClO₄, Cf₃SO₃,



in which R⁴ is hydrogen atom, an amino group, an anilino group, an alkyl group having 1 to 4 carbon atoms or an alkoxy group having 1 to 4 carbon atoms, each of R⁵ and R⁶ is independently an alkoxy group having 1 to 4 carbon atoms and R⁷ is hydrogen atom, an amino group, an anilino group, an alkyl group having 1 to 4 carbon atoms or an alkoxy group having 1 to 4 carbon atoms, iodonium salt of the formula (6)

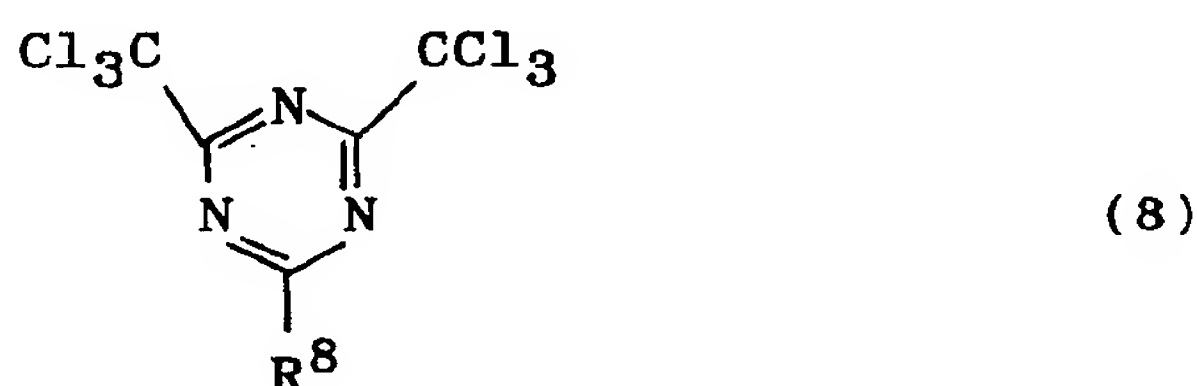


wherein R¹, R² and X are as defined in the above formula (5), and pyridinium salt of the formula (7)

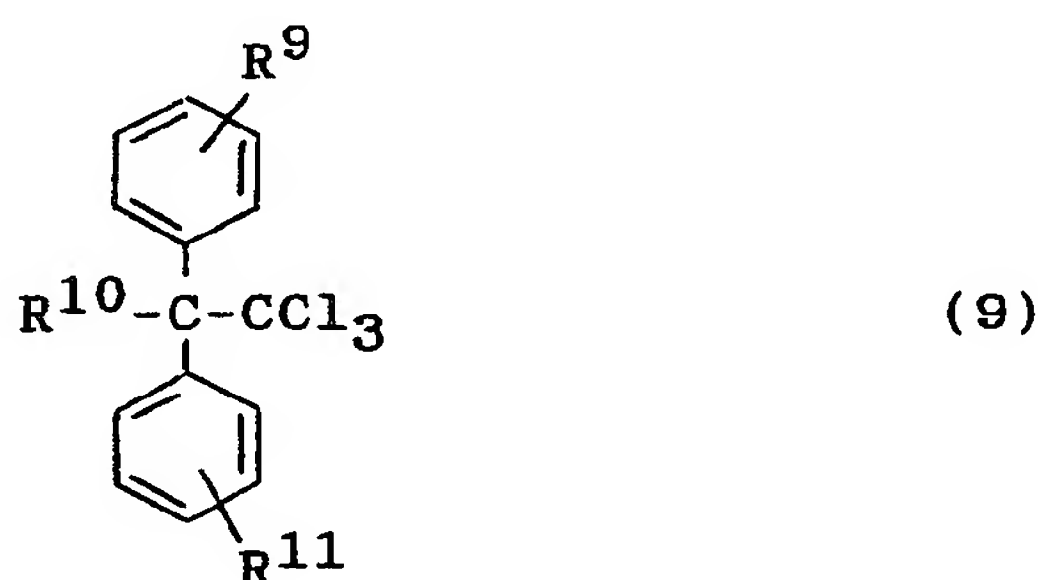


wherein R¹, R², R³ and X are as defined in the above formula (5).

Examples of the halogen-containing compound include a haloalkyl group-containing hydrocarbon compound and a haloalkyl group-containing heterocyclic compound. Preferred is at least one halogen-containing compound selected from the group consisting of a compound of the formula (8),

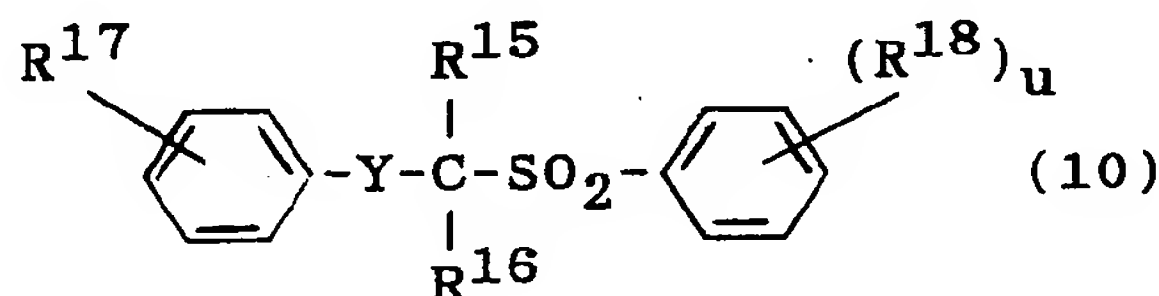


wherein R⁸ is a monovalent organic group such as trichloromethyl, phenyl, methoxyphenyl, naphthyl, methoxynaphthyl, chlorophenyl, methylenedioxyphenyl and styryl, and a compound of the formula (9),



wherein each of R⁹, R¹⁰ and R¹¹ is hydrogen atom, a halogen atom, a methyl group, a methoxy group or a hydroxyl group.

Examples of the sulfone compound include β-ketonesulfone and β-sulfonylsulfone. Preferred is a sulfone compound of the formula (10),

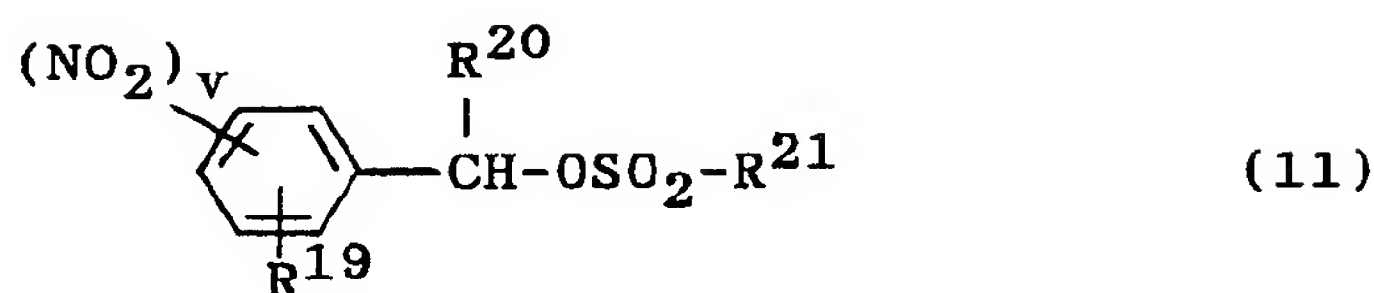


wherein Y is

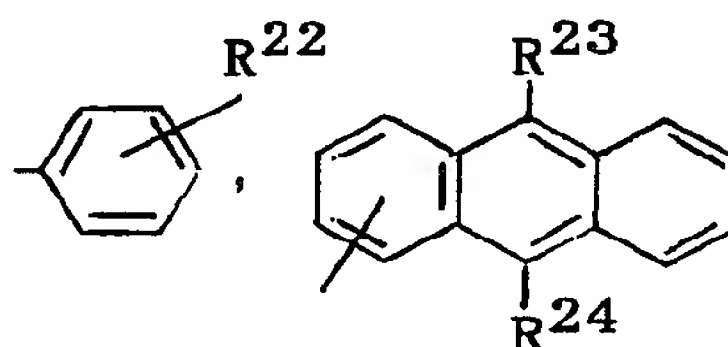


or -SO₂-, each of R¹⁵, R¹⁶, R¹⁷ and R¹⁸ is independently hydrogen atom, an alkyl group having 1 to 4 carbon atoms or a halogen atom, and u is an integer of 0 to 3.

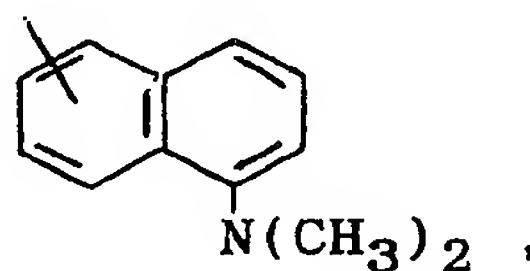
Examples of the nitrobenzyl compound include a nitrobenzylsulfonate compound and a dinitrobenzylsulfonate compound. Preferred is a nitrobenzyl compound of the formula (11),



wherein R^{19} is an alkyl group having 1 to 4 carbon atoms, R^{20} is hydrogen atom or a methyl group, R^{21} is



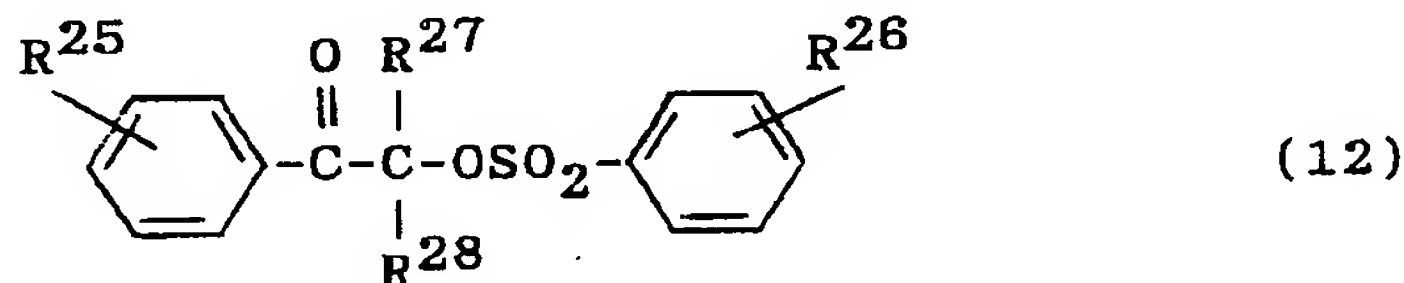
or



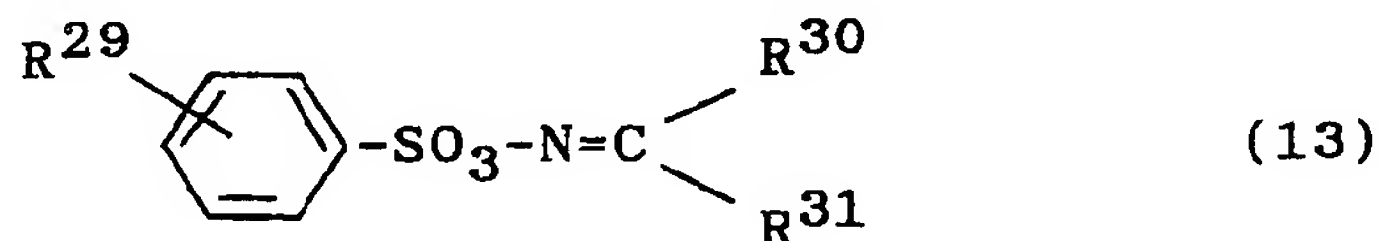
in which R^{22} is hydrogen atom or a methyl group and each of R^{23} and R^{24} is independently an alkoxy group having 1 to 4 carbon atoms, and v is an integer of 1 to 3.

Examples of the sulfonate compound include alkylsulfonic acid ester, haloalkylsulfonic acid ester, arylsulfonic acid ester and iminosulfonate.

Preferred is at least one sulfonate compound selected from the group consisting of a compound of the formula (12),



wherein each of R^{25} and R^{26} is independently hydrogen atom or an alkyl group having 1 to 4 carbon atoms, each of R^{27} and R^{28} is independently hydrogen atom, an alkyl group having 1 to 4 carbon atoms or an aryl group having 6 to 20 carbon atoms, a compound of the formula (13),



wherein R^{29} is hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and each of R^{30} and R^{31} is independently an alkyl group having 1 to 4 carbon atoms or an aryl group having 6 to 20 carbon atoms, or R^{30} and R^{31} may bond together to form a ring together with a carbon atom to which the R^{30} and R^{31} bond, and a compound of the formula (14),



wherein Z is an alkyl group having 1 to 4 carbon atoms, an aryl group having 6 to 20 carbon atoms, trifluoromethyl group or trichloromethyl group.

Among the above compounds, the onium salt is particularly preferred. The amount of the radiation-sensitive acid-forming agent per 100 parts by weight of the above resin (A) or resin (B) is preferably 1 to 70 parts by weight, more preferably 3 to 50 parts by weight, particularly preferably 3 to 20 parts by weight. When this amount is less than 1 part by weight, it is difficult to obtain sufficient pattern-formability. When it exceeds 70 parts by weight, scumming is liable to occur.

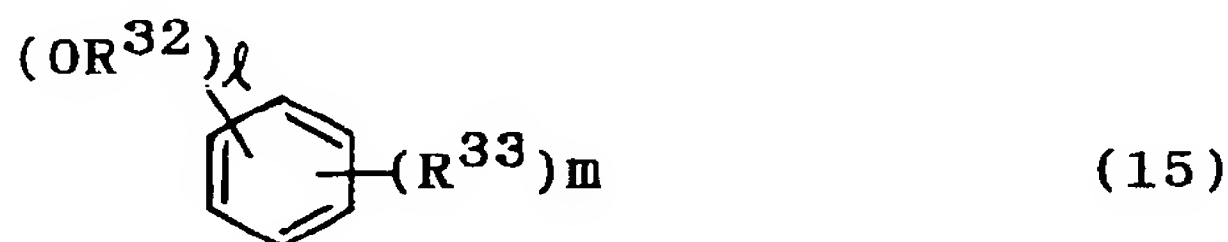
Solubility controller

The first resist coating composition contains a solubility controller. The solubility controller refers to a compound which has an effect of controlling the alkali solubility of an alkali-soluble resin and which is decomposed, e.g., hydrolyzed, in the presence of an acid to exhibit the property of reducing or losing the effect of controlling the alkali solubility or the property of promoting the alkali solubility of the resin (A).

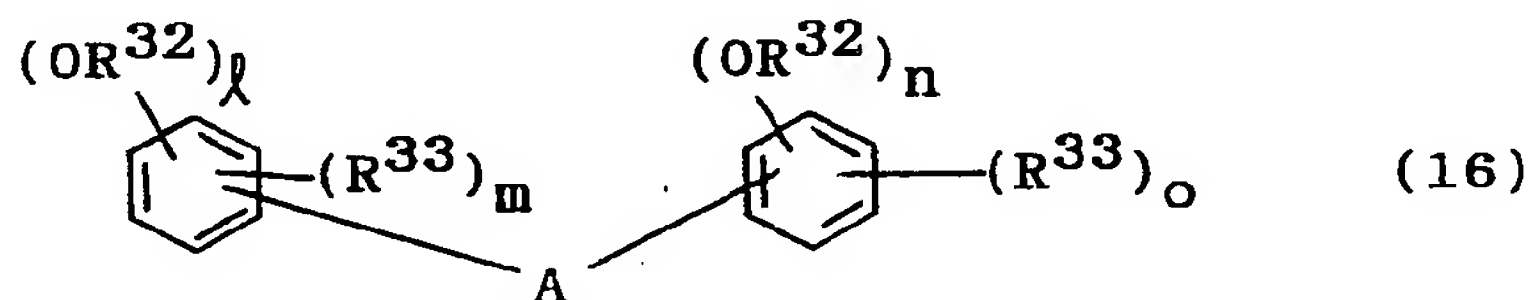
Examples of the solubility controller include compounds in which a substituent which can be freed in the presence of an acid is introduced into an acidic functional group. Although not specially limited, the above substituent includes the substituent B described regarding the above resin (B).

The above solubility controller may be either a low-molecular-weight compound or a high-molecular-weight compound.

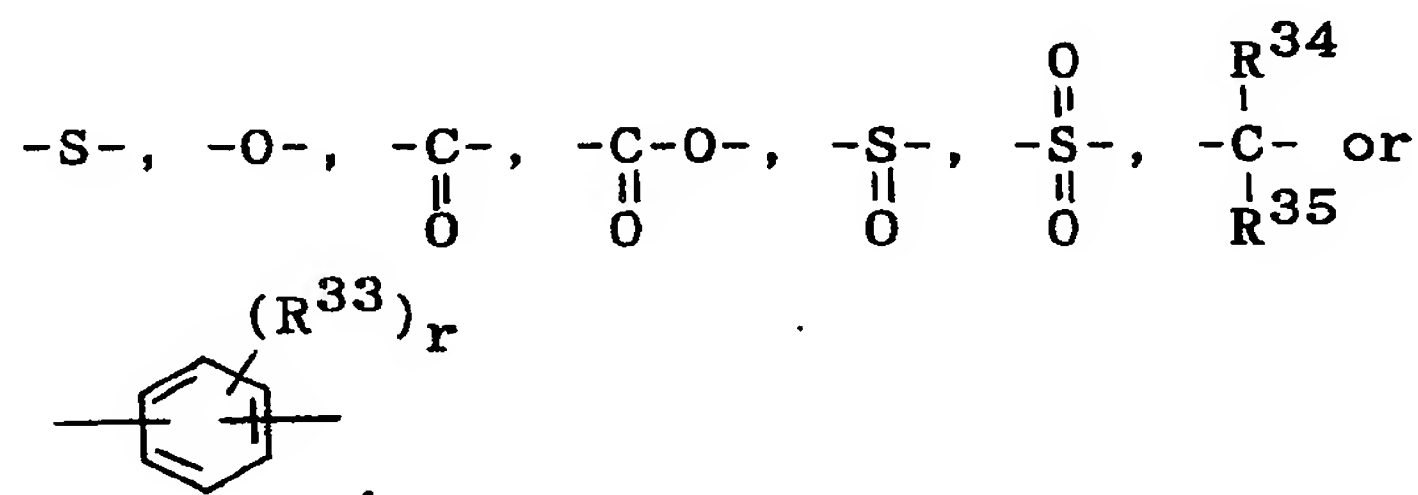
Examples of the solubility controller include a compound of the formula (15),



wherein each of R³² is independently at least one acid-decomposing group selected from a substituted methyl group, a 1-substituted ethyl group, a germyl group, a silyl group, an alkoxy carbonyl group and an acyl group, each of R³³s is independently an alkyl group having 1 to 4 carbon atoms, phenyl or naphthyl, and ℓ and m are integer of 0 or more which satisfy $\ell + m \leq 6$ and $1 \leq \ell$,
a compound of the formula (16),

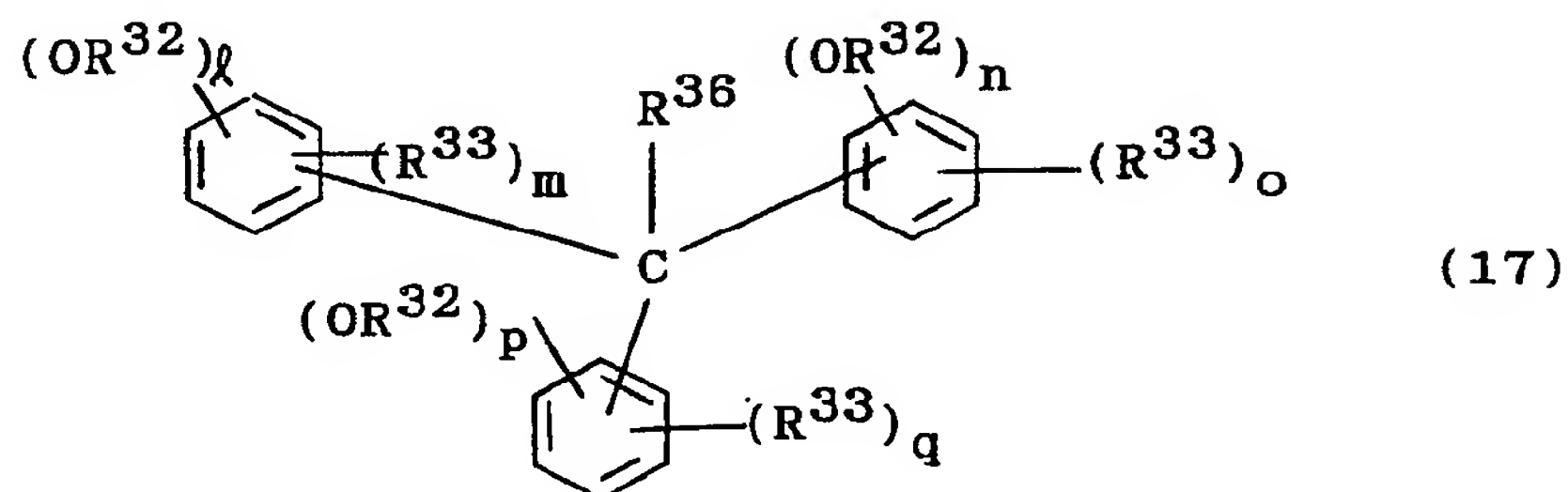


wherein R^{32} and R^{33} are as defined in the above formula (15), ℓ , m , n and o are integers of 0 or more which satisfy $\ell+m \leq 5$, $n+o \leq 5$ and $1 \leq \ell+n$,
and A is a single bond,

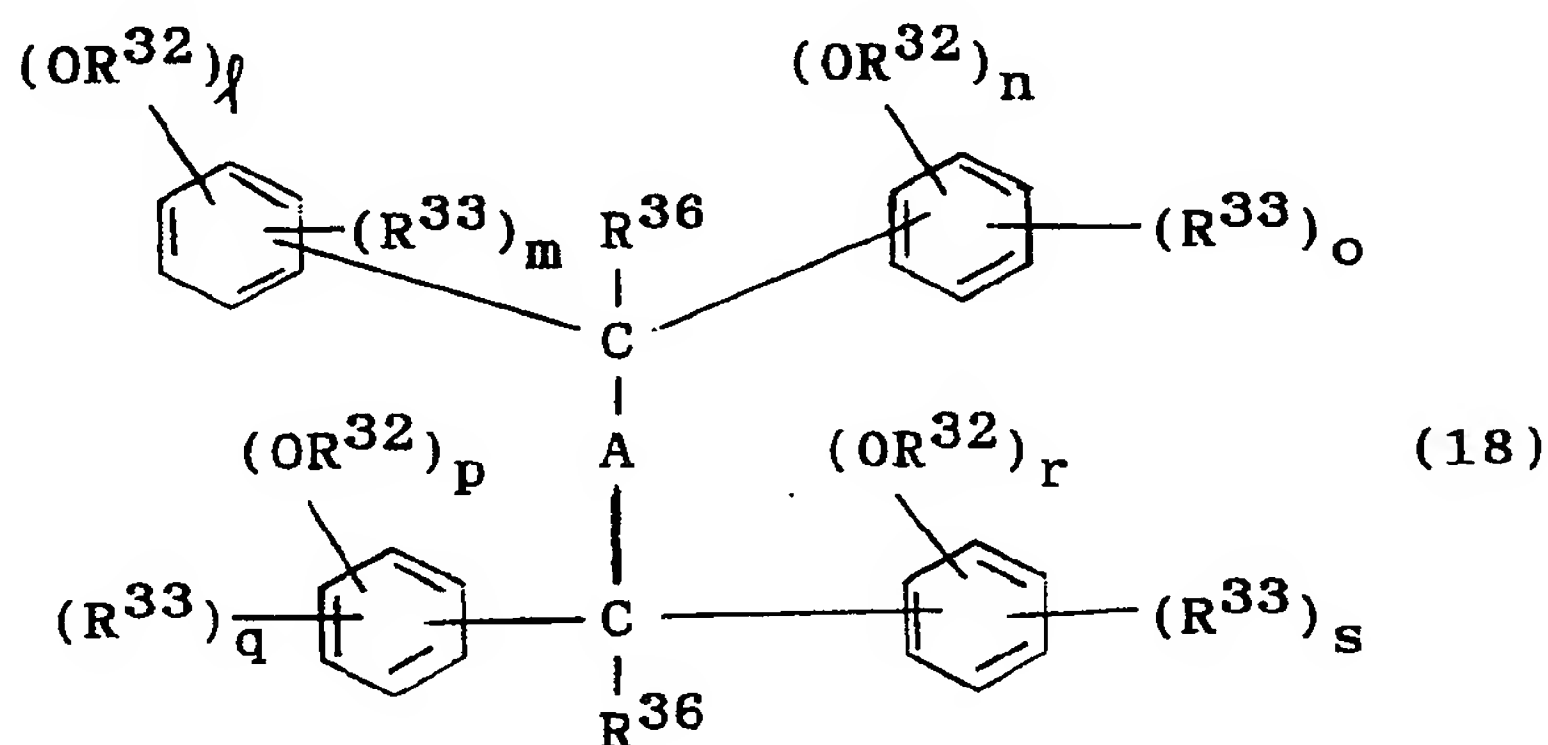


in which R³³ is as defined in the above formula (15) and each of R³⁴ and R³⁵ is independently hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an acyl group, a phenyl group or a naphthyl group and r is an integer satisfying 0 ≤ r ≤ 4,

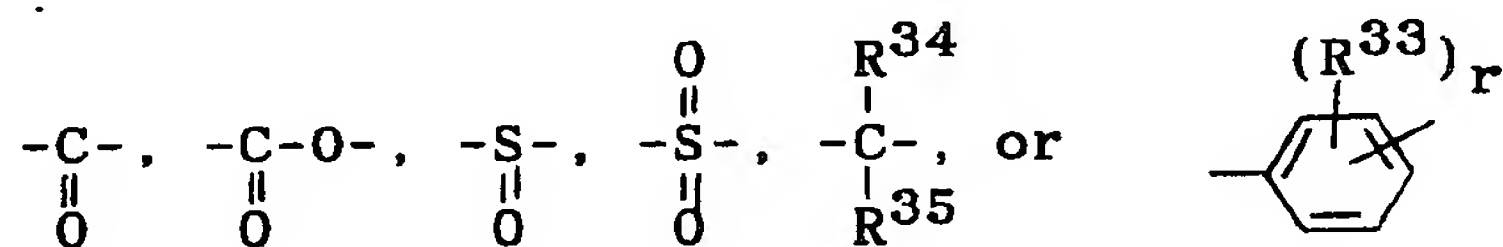
compound of the formula (17),



15 wherein R^{32} and R^{33} are as defined in the above formula (15), l , m , n , o , p and q are integers of 0 or more which satisfy $l+m \leq 5$, $o+n \leq 5$, $p+q \leq 5$ and $1 \leq l+n+p$, and R^{36} is hydrogen atom, an alkyl group having 4 carbon atoms or less or phenyl, a compound of the formula (18),



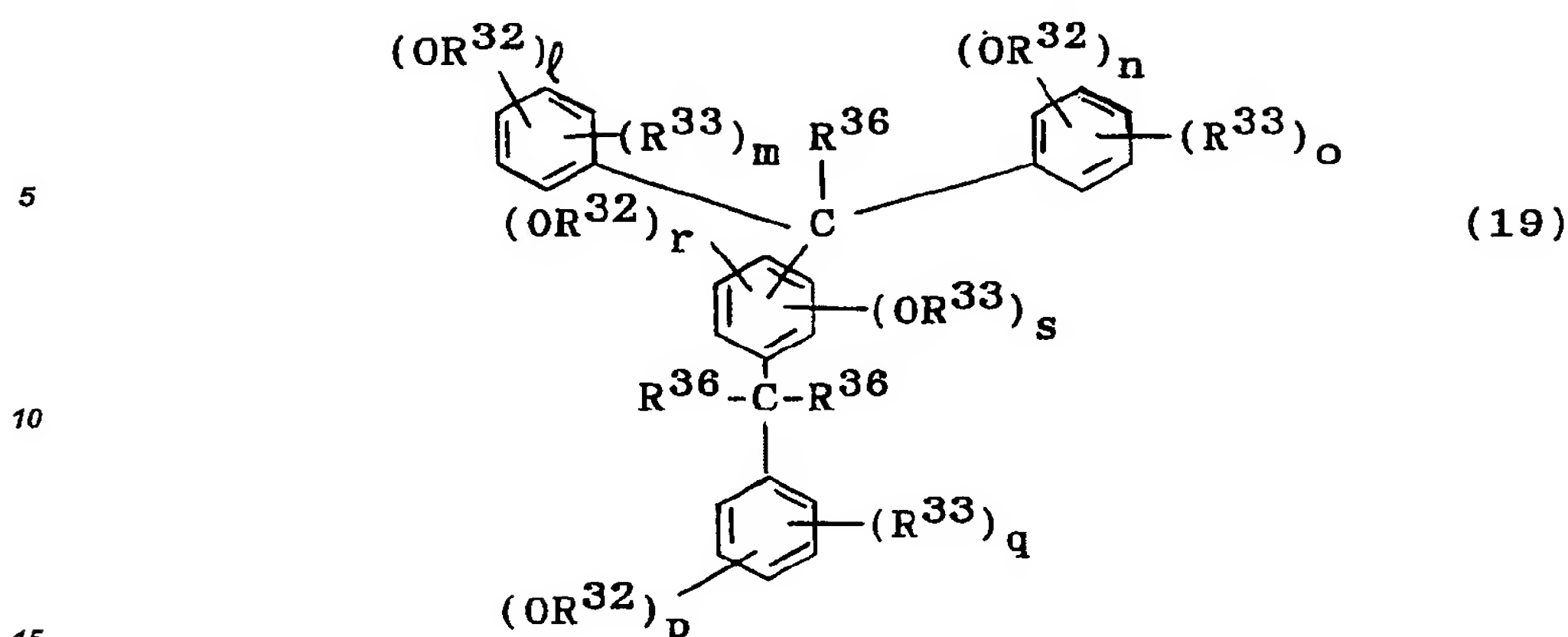
35 wherein R^{32} , R^{33} and R^{36} are as defined in the above formula (17), l , m , n , o , p , q and r are integers of 0 or more which satisfy $l+m \leq 5$, $n+o \leq 5$, $p+q \leq 5$, $r+s \leq 5$ and $1 \leq l+n+p+r$, and A is a single bond, $-S-$, $-O-$,



45 in which R^{33} , R^{34} , R^{35} and r are as defined in the above formula (16), and a compound of the formula (19),

50

55



wherein R^{32} , R^{33} and R^{36} are as defined in the above formula (17), and ℓ , m , n , o , p , q , r and s are integers of 0 or more which satisfy $\ell+m \leq 5$, $p+q \leq 5$, $n+o \leq 5$, $r+s \leq 4$ and $1 \leq \ell+n+r+p$.

Further, as the solubility controller (C), similarly advantageously usable is the same compound as the above resin (B), i.e., a resin which has at least one acid-decomposing group selected from a substituted methyl group, a 1-substituted ethyl group, a silyl group, a germyl group, an alkoxy carbonyl group and an acyl group and is insoluble or sparingly soluble in an alkali, and which is alkali-soluble when the above group is acid-decomposed.

In the first resist coating composition, the amount of the solubility controller per 100 parts by weight of the resin (A) is preferably 5 to 150 parts by weight, more preferably 5 to 100 parts by weight.

Crosslinking agent

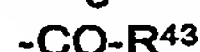
The third resist coating composition contains a crosslinking agent. This crosslinking agent is a compound which crosslinks the resin (A) in the presence of an acid, e.g., acid generated upon exposure to radiation.

The above crosslinking agent is not specially limited if it has the above property. As the crosslinking agent, preferred is, for example, an aromatic compound having a substituent which can undergo a crosslinking reaction.

Examples of the crosslinking agent, i.e., the (c') compound, include an aromatic compound having a group of the following formula,



wherein each of R^{37} and R^{38} is independently hydrogen atom or an alkyl group having 1 to 4 carbon atoms and R^{39} is hydrogen atom or an alkyl group having 1 to 5 carbon atoms, an aralkyl group having 7 to 20 carbon atoms, a group of $-\text{NR}^{40}\text{R}^{41}$ in which each of R^{40} and R^{41} is independently an alkyl group having 1 to 4 carbon atoms or a cyclo-ring of 3 to 8 atoms containing a hetero-atom or no hetero-atom, or a group of $-\text{COR}^{42}$ in which R^{42} is an alkyl group having 1 to 4 carbon atoms or an aryl group having 6 to 14 carbon atoms, an aromatic compound having a group of the following formula,

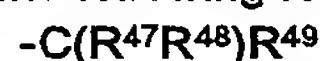


wherein R^{43} is hydrogen atom or an alkyl group having 1 to 4 carbon atoms, an aromatic compound having a group of the following formula,



wherein each of R^{44} , R^{45} and R^{46} is independently hydrogen atom or an alkyl group having 1 to 4 carbon atoms,

and an aromatic compound having a group of the following formula,



wherein each of R^{47} and R^{48} is independently hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and R^{49} is a three-membered ring which consists of either an oxygen atom or a divalent sulfur atom and of two carbon and hydrogen atoms and which may have a substituent having 1 to 3 carbon atoms.

Examples of the above group which can undergo a crosslinking reaction include a glycidyl ether group, a glycidyl ester group, glycidylamino group, methoxymethyl group, methylol group, ethoxymethyl group, benzyloxymethyl group, dimethylaminomethyl group, diethoxymethylamino group, morpholinomethyl group, acetoxymethyl group, benzoyloxymethyl group, formyl group, acetyl group, vinyl group and isopropenyl group.

Examples of the aromatic compounds having the above substituents include a bisphenol A epoxy com-

pound, a bisphenol F epoxy compound, a bisphenol S epoxy compound, a novolak epoxy compound, a resol
 resin epoxy compound, a polyhydroxystyrene epoxy compound, a methylol group-containing melamine resin,
 a methylol group-containing benzoguanamine resin, a methylol group-containing urea resin, a methylol group-
 containing phenolic resin, a methylol group-containing melamine compound, a methylol group-containing phe-
 5 nol compound, an alkoxy methyl group-containing melamine resin, an alkoxy methyl group-containing benzo-
 guanamine resin, an alkoxy methyl group-containing urea resin, an alkoxy methyl group-containing phenolic
 resin, an alkoxy methyl group-containing melamine compound, an alkoxy methyl group-containing phenol com-
 pound, a acetoxymethyl group-containing melamine resin, a acetoxymethyl group-containing benzoguan-
 amine resin, a acetoxymethyl group-containing urea resin, a acetoxymethyl group-containing phenolic resin, a
 10 acetoxymethyl group-containing melamine compound and a acetoxymethyl group-containing phenol com-
 pound.

Of the above aromatic compounds, preferred are a methylol group-containing phenolic resin, a methylol
 group-containing phenol compound, a methoxymethyl group-containing melamine compound, a methoxyme-
 15 thyl group-containing phenol compound and an acetoxymethyl group-containing phenol compound. More pre-
 ferred is a methoxymethyl group-containing melamine compound. Specific examples of said compound in-
 clude CYMEL 300, CYMEL 301, CYMEL 303 and CYMEL 305, all supplied by Mitsui Cyanamid Ltd.

Further, as the crosslinking agent, there can be used a modification product of the resin (A), which is a
 product imparted with the property of a crosslinking agent by modifying the resin (A) with the above substituent
 which can undergo a crosslinking agent. In this case, the above substituent is introduced in such an amount
 20 that the amount of the introduced substituent based on the total amount of the acidic functional group of the
 resin (A) is generally 5 to 60 %. preferably 10 to 50 %, more preferably 15 to 40 %. When the above amount
 is less than 5 %, undesirably, it is difficult to achieve a sufficient crosslinking reaction, and as a result, the
 ratio of the remaining coating declines and the pattern is liable to have a non-uniform line breadth and swell.
 When it exceeds 60 %, the alkali solubility of the resin (A) tends to decrease to deteriorate developability.

25 The amount of the crosslinking agent per 100 parts by weight of the resin (A) is preferably 5 to 95 parts
 by weight, particularly preferably 15 to 85 parts by weight, further particularly preferably 20 to 75 parts by
 weight. When this amount is less than 5 parts by weight, it is difficult to achieve a sufficient crosslinking re-
 action, and as a result, the ratio of a remaining coating decreases and the pattern is liable to have a non-uniform
 line breadth and swell. When it exceeds 95 %, scumming tends to occur to a great extent to deteriorate devel-
 30 opability.

Solvent

The solvent is selected from MMP, EEP or a mixture of these.

35 The above solvent imparts the first, second and third resist coating compositions with an excellent storage
 stability, and can provide these resist coating compositions with the property of being capable of giving ex-
 cellent resist sensitivity and an excellent form of a pattern with good reproducibility even after a prepared resist
 solution is stored for a long period of time.

The amount of the solvent per 100 parts by weight of the resin (A) or (B) is generally 20 to 3,000 parts by
 40 weight, preferably 50 to 3,000 parts by weight, more preferably 100 to 2,000 parts by weight.

In the present invention, other solvent may be added to the solvent of MMP and/or EEP. The amount of
 the other solvent based on the total solvent amount is, for example, less than 70 % by weight, preferably less
 than 50 % by weight, particularly preferably 30 % by weight.

The above "other solvent" include a compound of the formula (i),



45 wherein R^{50} is hydrogen atom or a monovalent hydrocarbon group having 1 to 4 carbon atoms, R^{51} is a
 divalent or trivalent hydrocarbon group having 1 to 4 carbon atoms, R^{52} is a monovalent hydrocarbon group
 having 1 to 4 carbon atoms and n is 1 or 2, provided that the case where R^{50} and R^{52} are methyl and R^{51} is a
 divalent C_2 hydrocarbon is excluded and that the case where R^{50} and R^{52} are ethyl and R^{51} is a divalent C_2
 50 hydrocarbon is excluded.

The monovalent hydrocarbon group having 1 to 4 carbon atoms is preferably selected from an linear or
 branched alkyl group. The divalent or trivalent hydrocarbon group having 1 to 4 carbon atoms is preferably se-
 lected from a divalent or trivalent, linear or branched aliphatic hydrocarbon group.

Specific examples of the above compound include alkyl hydroxyacetates such as methyl hydroxyacetate,
 55 methyl methoxyacetate, methyl ethoxyacetate, methyl propoxyacetate, methyl butoxyacetate, ethyl hydrox-
 yacetate, ethyl methoxyacetate, ethyl ethoxyacetate, ethyl propoxyacetate, ethyl butoxyacetate, propyl pro-
 poxyacetate and butyl butoxyacetate, and derivatives of these; alkyl 2-hydroxypropionates such as methyl 2-
 hydroxypropionate, methyl 2-methoxypropionate, methyl 2-ethoxypropionate, methyl 2-propoxypropionate,

methyl 2-butoxypropionate, ethyl 2-hydroxypropionate, ethyl 2-methoxypropionate, ethyl 2-ethoxypropionate, ethyl 2-propoxypropionate, ethyl 2-butoxypropionate, propyl 2-propoxypropionate and butyl 2-butoxypropionate, and derivatives of these; alkyl 3-hydroxypropionates such as methyl 3-hydroxypropionate, methyl 3-ethoxypropionate, methyl 3-propoxypropionate, methyl 3-butoxypropionate, ethyl 3-hydroxypropionate, ethyl 3-methoxypropionate, ethyl 3-propoxypropionate, ethyl 3-butoxypropionate, propyl 3-propoxypropionate and butyl 3-butoxypropionate, and derivatives of these; alkyl 3,3-dihydroxypropionates such as methyl 3,3-dihydroxypropionate, methyl 3,3-dimethoxypropionate, methyl 3,3-diethoxypropionate, methyl 3,3-dipropoxypropionate, methyl 3,3-dibutoxypropionate, ethyl 3,3-dihydroxypropionate, ethyl 3,3-dimethoxypropionate, ethyl 3,3-diethoxypropionate, ethyl 3,3-dipropoxypropionate and ethyl 3,3-dibutoxypropionate, and derivatives of these; alkyl 4-hydroxybutyrates such as methyl 4-hydroxybutyrate, methyl 4-methoxybutyrate, methyl 4-ethoxybutyrate, methyl 4-propoxybutyrate, ethyl 4-hydroxybutyrate, ethyl 4-methoxybutyrate, ethyl 4-ethoxybutyrate and ethyl 4-propoxybutyrate, and derivatives of these; alkyl 4,4-dihydroxybutyrates such as methyl 4,4-dihydroxybutyrate, methyl 4,4-dimethoxybutyrate, methyl 4,4-diethoxybutyrate, methyl 4,4-dipropoxybutyrate, methyl 4,4-dihydroxybutyrate, ethyl 4,4-dimethoxybutyrate, ethyl 4,4-diethoxybutyrate and ethyl 4,4-dipropoxybutyrate, and derivatives of these; alkyl 5-hydroxyvalerates such as methyl 5-methoxyvalerate, methyl 5-hydroxyvalerate, methyl 5-ethoxyvalerate, methyl 5-propoxyvalerate, ethyl 5-hydroxyvalerate, ethyl 5-methoxyvalerate, ethyl 5-ethoxyvalerate and ethyl 5-propoxyvalerate, and derivatives of these; and alkyl 5,5-dihydroxyvalerates such as methyl 5,5-dihydroxyvalerate, methyl 5,5-dimethoxyvalerate, methyl 5,5-diethoxyvalerate, methyl 5,5-dipropoxyvalerate, ethyl 5,5-dihydroxyvalerate, ethyl 5,5-dimethoxyvalerate, ethyl 5,5-diethoxyvalerate and ethyl 5,5-dipropoxyvalerate, and derivatives of these.

In addition to the compound of the above formula (i), examples of the "other solvent" include ethers such as diethylene glycol dimethyl ether, diethylene glycol diethyl ether, benzyl ethyl ether and dihexyl ether; esters such as methyl pyruvate, ethyl pyruvate, ethyl acetate, butyl acetate, benzyl acetate, ethyl benzoate, diethyl oxalate, diethyl maleate, ethylene carbonate, propylene carbonate and γ -butyrolactone; ketones such as methyl ethyl ketone, cyclohexanone, diisobutyl ketone, acetonyl acetone, isophorone, 2-heptanone, 3-heptanone and 4-heptanone; amides such as N-methylpyrrolidone, N,N-dimethylformamide and N,N-dimethylacetamide; alcohols such as 1-octanol, 1-nonanol and benzyl alcohol; monoethers of diols such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether and diethylene glycol monoethyl ether; and ether esters of diols such as ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether acetate and propylene glycol monoethyl ether acetate.

The compositions of the present invention may further contain a variety of additives as required.

Examples of the additives include surfactants for improving the coatability and the developability of an irradiated portion of a formed and dried coating and for reducing the striation. Examples of the surfactants include polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octyl phenol ether, polyoxyethylene nonyl phenol ether, polyethylene glycol dilaurate, polyethylene glycol distearate and commercially available products such as Eftop EF301, EF303 and EF352 (supplied by Tohken Products Ltd.), Megafac F171 and F173 (supplied by Dainippon Ink & Chemicals Inc.), Fluorad FC430 and FC431 (supplied by Sumitomo 3M Co., Ltd.), Asahi Guard AG710 and Surflon S-382, SC101, SC102, SC103, SC104, SC105 and SC106 (supplied by Asahi Glass Co., Ltd.), KP341 (supplied by Shin-Etsu Chemical Co., Ltd.), and Polyflow No. 75 and No. 95 (supplied by Kyoisha Oils and Fats Co., Ltd.).

The amount of the surfactant per 100 parts by weight of the resin (A) or (B) is generally 2 parts by weight or less.

Examples of other additives include an azo-containing compound, a halation preventer composed of an amine-containing compound, an adhesion aid, a storage stabilizer and an antifoamer.

Each of the compositions of the present invention can be prepared by dissolving necessary amounts of the above resin (A) or (B), the radiation-sensitive acid-forming agent and optionally, other additives to be added as required, in the above solvent.

Each of the compositions of the present invention is applied onto a substrate such as a silicone wafer, etc., in the above solution form and dried to form a resist coating. For applying the solution onto the substrate, for example, the solution of the composition of the present invention is prepared, filtered, and then applied onto the substrate by spin coating, curtain flow coating or roll coating.

The so-formed resist coating is partly irradiated with radiation to form a fine pattern. The radiation is not specially limited, and can be selected from ultraviolet light such as i-ray, far ultraviolet light from an excimer laser, X ray such as synchrotron radiation, and charged corpuscular beam such as electron beam, depending upon the kind of a used radiation-sensitive acid-forming agent. The irradiation conditions such as a radiation dose are properly determined depending upon the components and mixing ratio of the composition and kinds of various additives.

In the present invention, it is preferred to carry out heating after the irradiation with radiation for improving the apparent sensitivity, etc., of the resist. Although differing depending upon the components and mixing ratio of the composition, the heating temperature is generally 30 to 200°C, preferably 50 to 150°C.

The developer solution used for the development at a next step is selected from alkaline solutions containing sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate, aqueous ammonia, ethylamine, n-propylamine, diethylamine, di-n-propylamine, triethylamine, methyldiethylamine, dimethylethanolamine, triethanolamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, pyrrole, piperidine, 1,8-diazabicyclo[5.4.0]-7-undecene and 1,5-diazabicyclo-[4.3.0]-5-nonane.

As a developer solution, there may be also used an alkaline aqueous solution prepared by adding a water-soluble organic solvent such as an alcohol, i.e., methanol or ethanol and a surfactant to the above developer solution.

The resist coating composition of the present invention is suitable as a resist coating composition which is excellent storage stability and is capable of giving a good pattern form. The resist coating composition of the present invention is suitable for use with any radiation including ultraviolet light such as i-ray, far ultraviolet light from an excimer laser, X-ray such as synchrotron radiation and charged corpuscular beam such as electron beam. Therefore, it can be advantageously used as a resist for producing semiconductor devices which are expected to become much finer.

The present invention will be detailed hereinafter by reference to Examples. However, the present invention shall not be limited by the Examples.

In Examples, various properties were measured as follows.

Mw

Measured by a gel permeation chromatography using GPC columns (two G2000H_{XL} columns, one G3000H_{XL} column and one G4000_{XL} column) supplied by Tosoh Corp and monodisperse polystyrene as a standard under the analysis conditions where the flow rate was 1.0 ml/minute, the elution solvent was tetrahydrofuran and the column temperature was 40°C.

Sensitivity

The radiation dose at which a line and space pattern having a line and space breadth of 0.5 μm could be formed as designed was taken as sensitivity. The unit was mJ/cm².

Amount of remaining coating

The resist coating thickness before and after the development was measured with Alpha-Step supplied by TENCOR, and the amount was calculated.

Synthesis Example 1

30 Grams of polyhydroxyethylene was dissolved in tetrahydrofuran, and 10 g of t-butoxypotassium was added. While the mixture was stirred at 0°C, 60 g of di-t-butylidicarbonate was added dropwise, and the mixture was allowed to react for 4 hours. After the reaction finished, the reaction mixture was added dropwise to water to precipitate a resin, and the precipitated resin was dried in a vacuum dryer at 50°C overnight. The resin had Mw of 15,000, and the result of NMR measurement showed that the resin had a structure in which 29 % of hydrogen atoms of phenolic hydroxyl group were replaced with t-butoxycarbonyl group. This resin is referred to as "resin I" hereinafter.

Synthesis Example 2

54 Grams of polyhydroxystyrene was dissolved in acetone, and 27 g of t-butyl-α-bromoacetate, 10 g of potassium carbonate and 9 g of potassium iodide were added. While refluxed with stirring, the mixture was allowed to react for 7 hours. After the reaction finished, the reaction mixture was added dropwise to water to precipitate a resin, and the precipitated resin was dried in a vacuum dryer at 50°C overnight. The resin had Mw of 18,000, and the result of NMR measurement showed that the resin had a structure in which 22 % of hydrogen atoms of phenolic hydroxyl group were replaced with t-butyl acetate residue. This resin is referred to as "resin 11" hereinafter.

Synthesis Example 3

36 Grams of polyhydroxystyrene was dissolved in ethyl acetate, and 30 g of 3,4-dihydro-2H-pyran and 0.1 g of p-toluenesulfonic acid were added. The mixture was allowed to react at 5°C for 4 hours with stirring. The reaction mixture was mixed with distilled water, and p-toluenesulfonic acid was extracted with a separating funnel. The remainder was added dropwise to hexane to precipitate a resin, and the precipitated resin was dried in a vacuum dryer at 50°C overnight. The resin had Mw of 14,000, and the result of NMR measurement showed that the resin had a structure in which 28 % of phenolic hydroxyl group was replaced with tetrahydropyranyl group. This resin is referred to as "resin III" hereinafter.

Synthesis Example 4

36 Grams of polyhydroxystyrene was dissolved in ethyl acetate, and 14 g of hexamethyldisilazane was added. The mixture was allowed to react under reflux for 6 hours, and then the reaction mixture was dried to solidness under reduced pressure. The resultant resin had Mw of 23,000, and the result of NMR measurement showed that the resin had a structure in which 49 % of phenolic hydroxyl group was replaced with trimethylsilyl group. This resin is referred to as "resin IV" hereinafter.

Synthesis Example 5

Synthesis Example 4 was repeated except that 14 g of the hexamethyldisilazane was replaced with 33 g of tris(trimethylgermyl)amine to give a resin. The resin had Mw of 24,000, and the result of NMR measurement showed that the resin had a structure in which 52 % of phenolic hydroxyl group was replaced with trimethylgermyl group. This resin is referred to as "resin V" hereinafter.

Synthesis Example 6

36 Grams of polyhydroxystyrene was dissolved in acetone, and 6 g of acetyl chloride was added. Then, while the mixture was stirred, 8 g of triethylamine was gradually added at 5°C to allow the mixture to react. Then, the reaction mixture was filtered, and added dropwise to water to precipitate a resin. The resin was dried in a vacuum dryer at 50°C overnight. The resin had Mw of 19,000, and the result of NMR measurement showed that the resin had a structure in which 24 % of phenolic hydroxyl group was replaced with acetyl group. This resin is referred to as "resin VI" hereinafter.

Synthesis Example 7

300 Grams of p-t-butoxystyrene, 30 g of styrene and 1.6 g of azobisisobutyronitrile were dissolved in 330 g of dioxane. The mixture was allowed to react under nitrogen atmosphere for 12 hours while the inside temperature was maintained at 70°C. After the reaction finished, unreacted monomers were removed by residimentation to obtain a poly(p-t-butoxystyrene/styrene) copolymer resin. Subsequently, the resin was hydrolyzed with an acid to give 180 g of poly(p-hydroxystyrene/styrene) copolymer resin having MW of 18,000. NMR showed that the copolymer ratio of p-hydroxystyrene to styrene was 85 to 15 (molar ratio). This resin is referred to as "resin VII" hereinafter.

Synthesis Example 8

15 Grams of hydroquinone was dissolved in tetrahydrofuran, and di-t-butyl dicarbonate whose amount was twice as large as the molar amount of the entirety of acid group thereof and triethylamine whose amount was 3/10 of the entirety of acid group thereof were added. Under reflux, the mixture was allowed to react for 6 hours. Then, the reaction mixture was added dropwise to water to form a precipitate. The precipitate was dried in a vacuum dryer at 50°C overnight to give a solubility controller (a) shown later.

Synthesis Examples 9 - 12

Solubility controllers b to e shown later were prepared in the same manner as in Synthesis Example 8 except that the hydroquinone was replaced with compounds which were similar to those compounds shown as solubility controllers b to e but had hydrogen atoms in place of t-butoxycarbonyl groups.

Examples 1 - 22 and Comparative Examples 1 - 10

Components shown in Table 1 were dissolved in a solvent shown in Table 1. Then, foreign substances were removed from the mixture by microfiltration through a 0.2 m filter to obtain a resist coating composition.

5 The resist coating composition was spin-coated on a silicon wafer and baked at 100°C for 2 minutes, and the so-formed resist coating was exposed to radiation through a mask by means of a KrF excimer laser apparatus (MBK-400TL-N) supplied by Admont Science. Then, the resist coating was baked at 110°C for 2 minutes, developed with a solution of 2.38% of tetramethylammonium hydroxide in water at 23°C for 60 seconds and rinsed with water for 30 seconds to form a resist pattern. The above resist pattern formation was repeated
10 with regard to a resist coating composition just after its preparation and after the storage of 30 days. The results are shown in Table 1.

The mixing ratio (part by weight) of the components and solvent in each Example was as follows.

Examples 1, 3, 5 and Comparative Examples 1 and 6:- Resin: 100, Acid-forming agent: 1.5, Solvent: 420.

Examples 2, 4, 6 and 22:- Resin: 100, Acid-forming agent: 1.5, Solvent: 420.

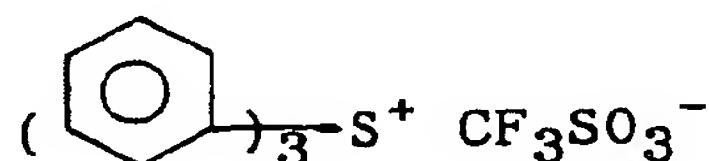
15 Examples 7 - 21 and Comparative Examples 2 - 5 and 7 - 10:- Resin: 100, Acid-forming agent: 3, Solubility controller or Crosslinking agent: 35, solvent: 400.

In Table 1, numerals 1 to 6 in the column of "Acid-forming agent" and alphabet letters a to i in the column of "Solubility controller or Crosslinking agent" show the following.

20 (I) Acid-forming agent

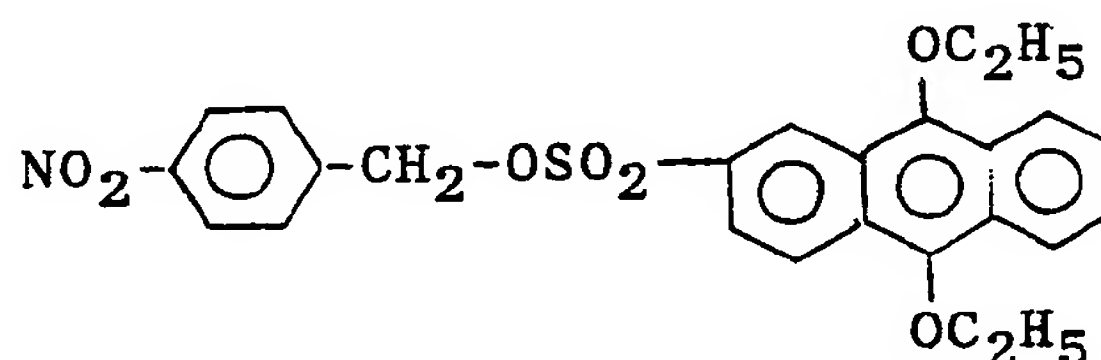
(1)

25



(2)

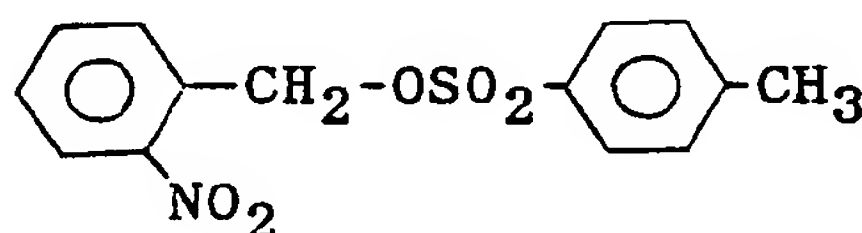
30



35

(3)

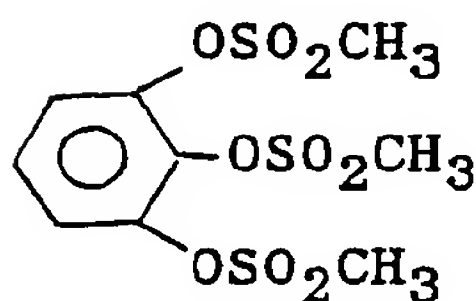
40



45

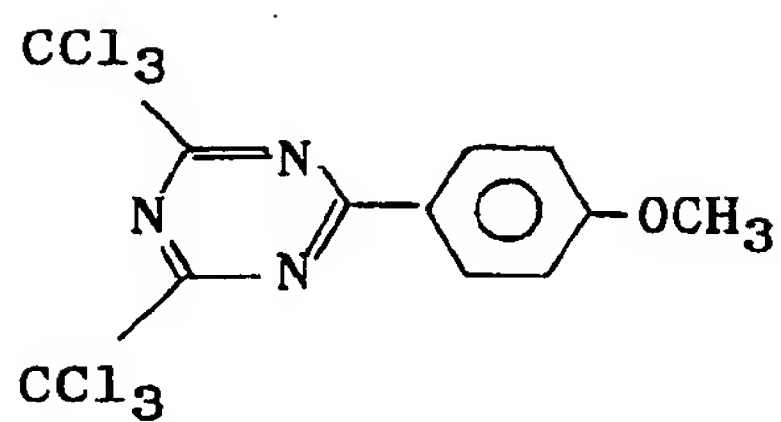
(4)

50

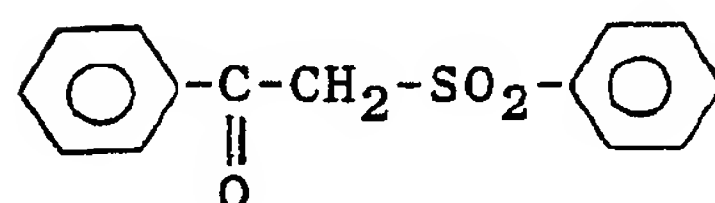


55

(5)

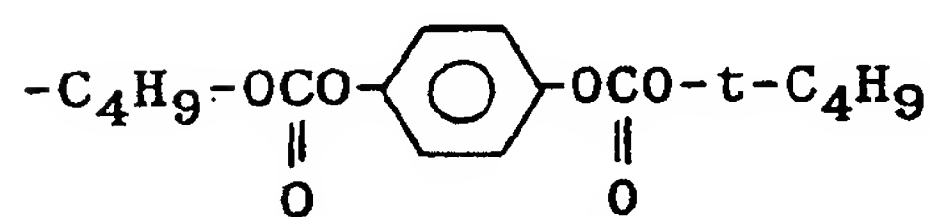


10 (6)

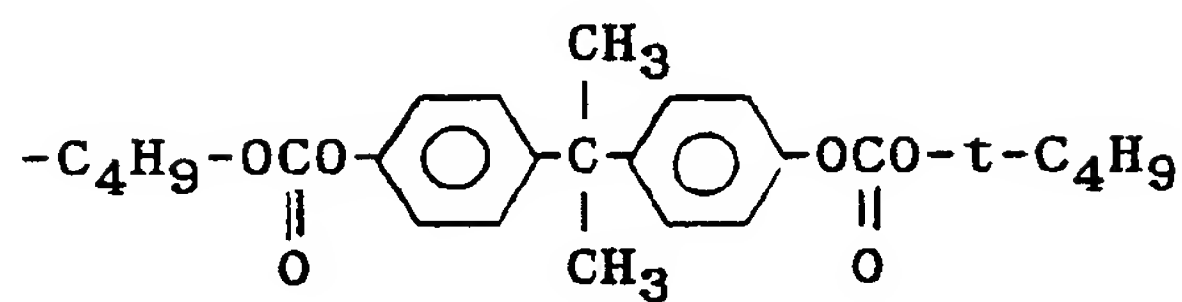


(II) Solubility controller

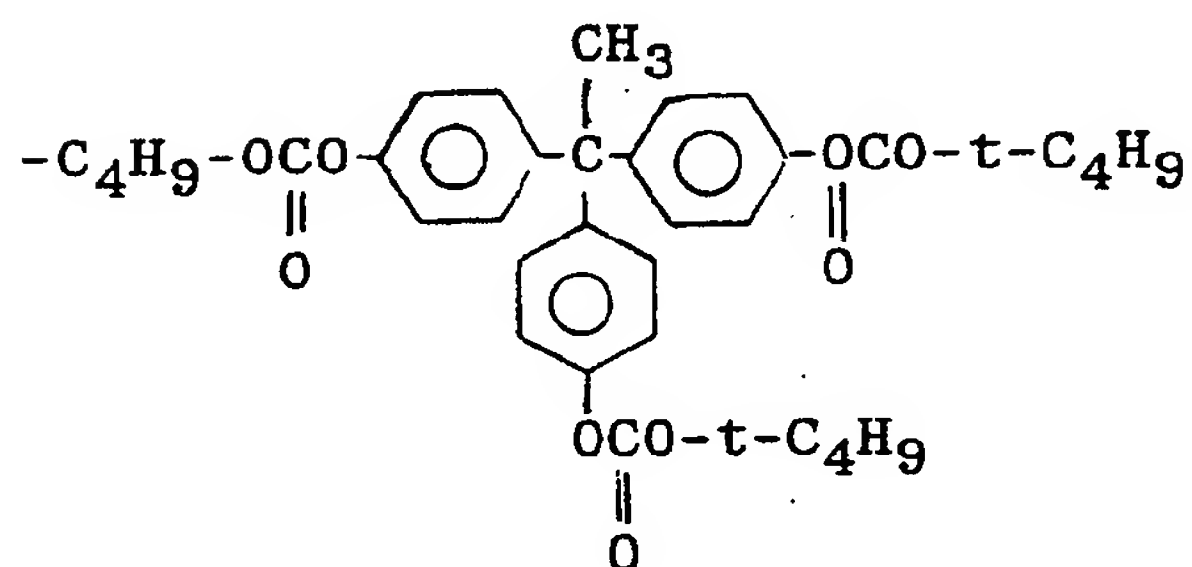
20 (a)



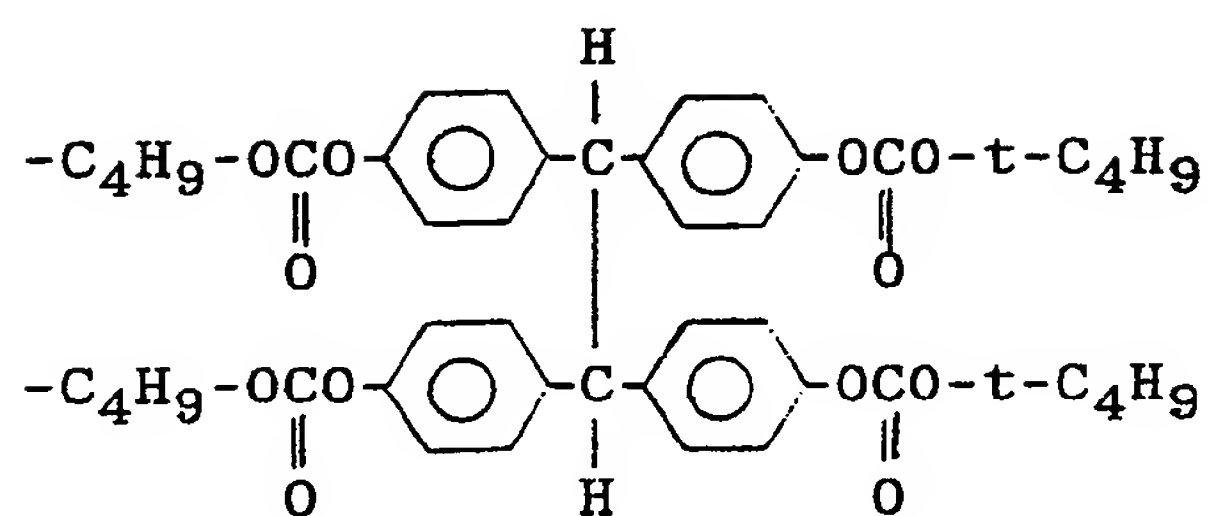
(b)



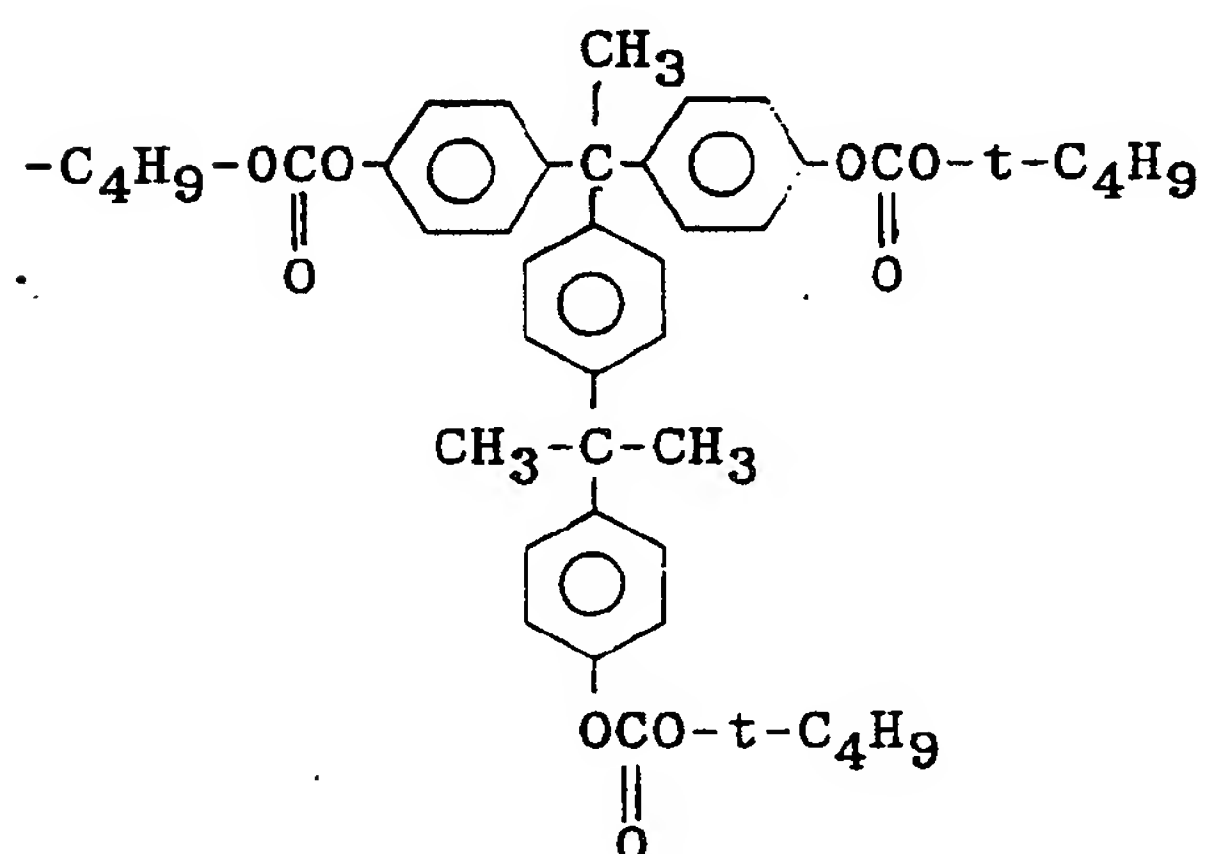
(c)



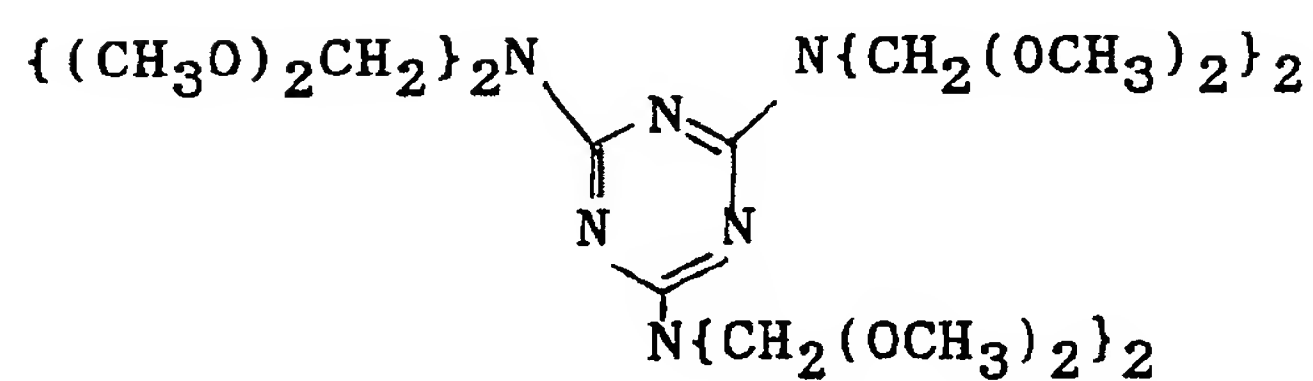
(d)



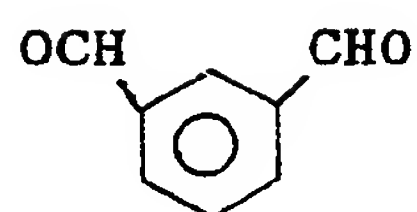
(e)

Crosslinking agent

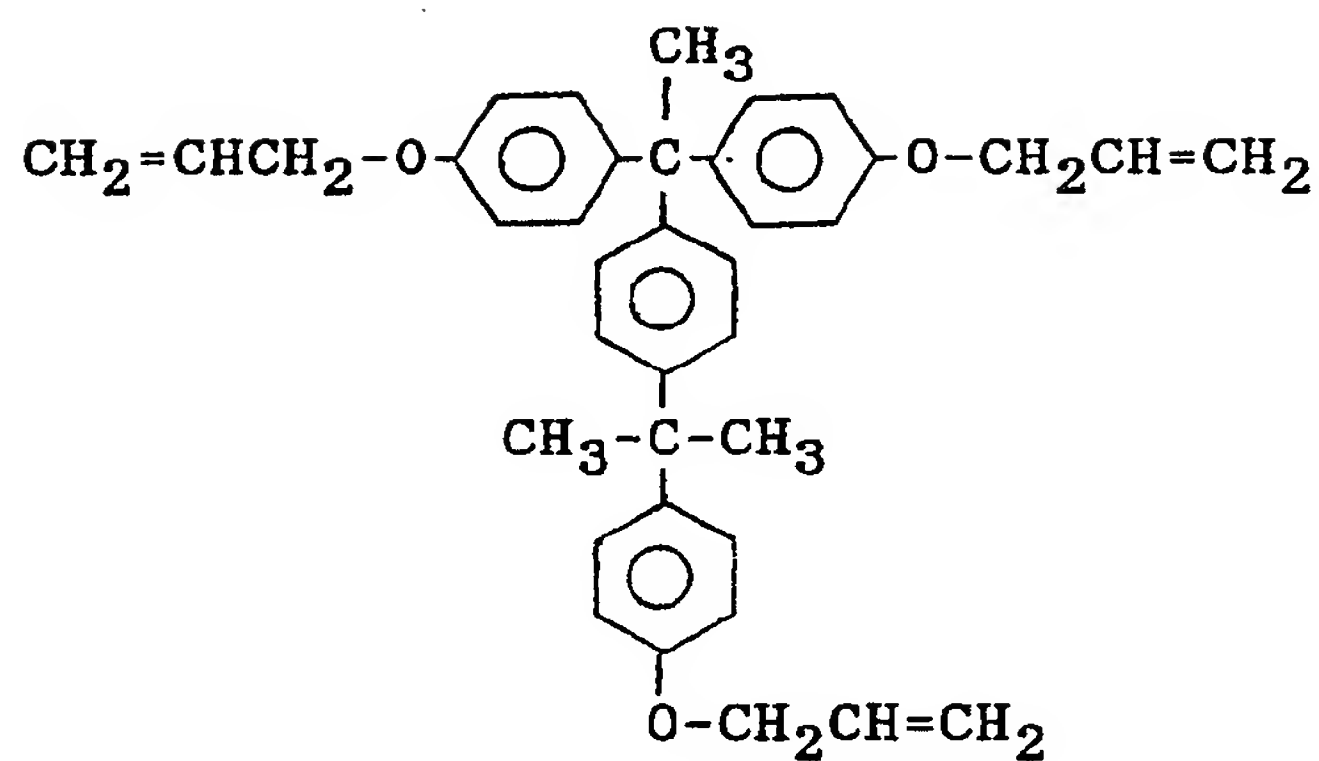
(f)



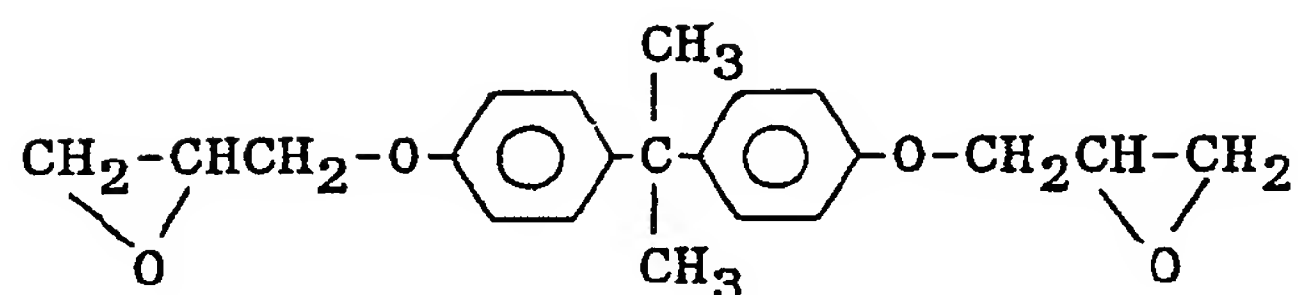
(g)



(h)



(i)

**(III) Solvent**

The following are abbreviations of the compounds for a solvent.

MMP: Methyl 3-methoxypropionate

EEP: Ethyl 3-ethoxypropionate

EL: Ethyl 2-oxypropionate

MEP: Ethyl 2-methoxypropionate

Table 1

| Example No. | Resin | Acid-form- ing agent | Solubility controller or Crosslink- agent | Solvent | Results of evaluation | | | | | Remark |
|-------------|-------|-------------------------|---|---------|--------------------------------------|------------------|-------------------------------------|------------------|--|--------|
| | | | | | Sensitivity (mJ/cm ²) | | Amount of remaining coating (μm) | | | |
| | | | | | As- prepared | After 30 days | As- prepared | After 30 days | | |
| | | | | | | | | | | |
| 1 | II | (1) | - | MMP | 20 | 20 | 0.02 | 0.02 | | |
| 2 | II | (2) | - | EEP | 34 | 34 | 0.02 | 0.02 | | |
| 3 | III | (1) | - | MMP | 50 | 52 | 0.01 | 0.01 | | |
| 4 | IV | (6) | - | EEP | 58 | 58 | 0.03 | 0.03 | | |
| 5 | V | (1) | - | MMP | 14 | 12 | 0.03 | 0.04 | | |
| 6 | VI | (1) | - | EEP | 84 | 82 | 0.02 | 0.02 | | |
| 7 | VII | (1) | b | MMP | 30 | 30 | 0.05 | 0.05 | | |
| 8 | VII | (5) | b | MMP | 96 | 96 | 0.05 | 0.04 | | |
| 9 | VII | (4) | b | MMP | 46 | 44 | 0.05 | 0.06 | | |
| 10 | VII | (3) | b | MMP | 38 | 36 | 0.05 | 0.07 | | |
| 11 | VII | (6) | b | MMP | 82 | 82 | 0.06 | 0.05 | | |
| 12 | VII | (1) | a | EEP | 20 | 20 | 0.12 | 0.14 | | |
| 13 | VII | (1) | c | EEP | 36 | 38 | 0.05 | 0.06 | | |
| 14 | VII | (1) | d | MMP | 34 | 34 | 0.05 | 0.04 | | |
| 15 | VII | (1) | e | MMP | 50 | 50 | 0.01 | 0.01 | | |
| 16 | VII | (1) | f | EEP | 36 | 36 | 0.08 | 0.08 | | |
| 17 | VII | (1) | g | EEP | 68 | 70 | 0.13 | 0.11 | | |

-to be continued -

Table 1 (continued)

| Example No. | Resin | Acid-form- ing agent | Solubility controller or Crosslink- ing agent | Solvent | Results of evaluation | | | | | Remark |
|-----------------------|-------|-------------------------|---|----------|--------------------------------------|------------------|-------------------------------------|------------------|------|--------|
| | | | | | Sensitivity (mJ/cm ²) | | Amount of remaining coating (μm) | | | |
| | | | | | As- prepared | After 30 days | As- prepared | After 30 days | | |
| | | | | | | | | | | |
| 18 | VII | (1) | h | EEP | 70 | 70 | 0.11 | 0.10 | | |
| 19 | VII | (1) | i | MMP | 42 | 42 | 0.08 | 0.08 | | |
| 20 | VII | (5) | f | MMP | 20 | 20 | 0.04 | 0.04 | | |
| 21 | VII | (5) | f | note (1) | 22 | 18 | 0.04 | 0.03 | | |
| 22 | II | (2) | - | note (2) | 36 | 36 | 0.02 | 0.03 | | |
| Comp. Example 1 | I | (1) | - | EL | 16 | 10 | 0.03 | 0.09 | | |
| | VII | (1) | b | EL | 34 | 22 | 0.05 | 0.23 | | |
| | VII | (1) | e | EL | 46 | 34 | 0.02 | 0.08 | | |
| | VII | (1) | f | EL | 34 | 24 | 0.08 | 0.06 | | |
| | VII | (5) | f | EL | 22 | 14 | 0.04 | 0.02 | | |
| | I | (1) | - | MEP | 24 | 20 | 0.02 | 0.04 | * | |
| | VII | (1) | b | MEP | 28 | 22 | 0.04 | 0.07 | * | |
| | VII | (1) | e | MEP | 44 | 52 | 0.02 | 0.02 | *** | |
| | VII | (1) | f | MEP | 36 | 32 | 0.07 | 0.12 | ** | |
| | 10 | VII | (5) | f | MEP | 20 | 14 | 0.04 | 0.01 | *** |

In the above Table,

note (1): MMP/EL = 50/50 (wt.)

note (2): MMP/EEP = 60/40 (wt.)

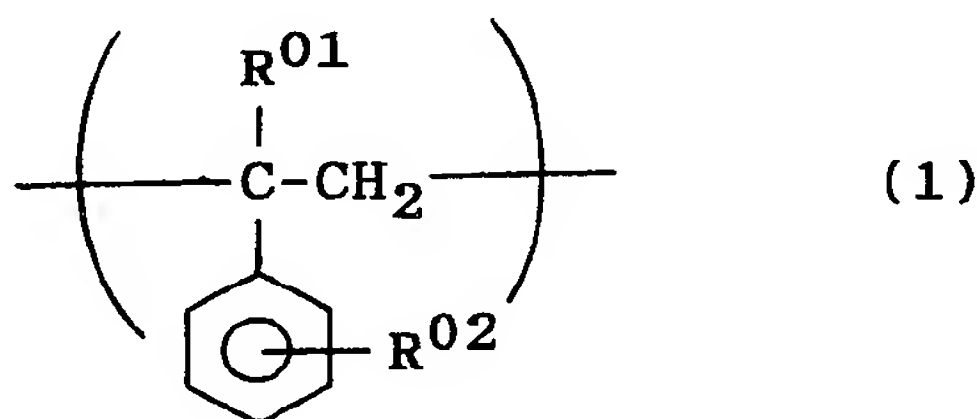
*) Coating unevenness was observed on the resist pattern formed after 30 days.

**) Scumming was observed on the resist pattern formed after 30 days.

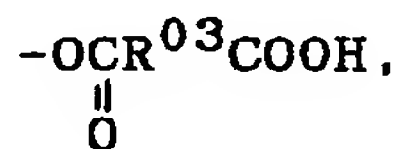
***) Coating unevenness and scumming were observed on the resist pattern formed after 30 days.

Claims

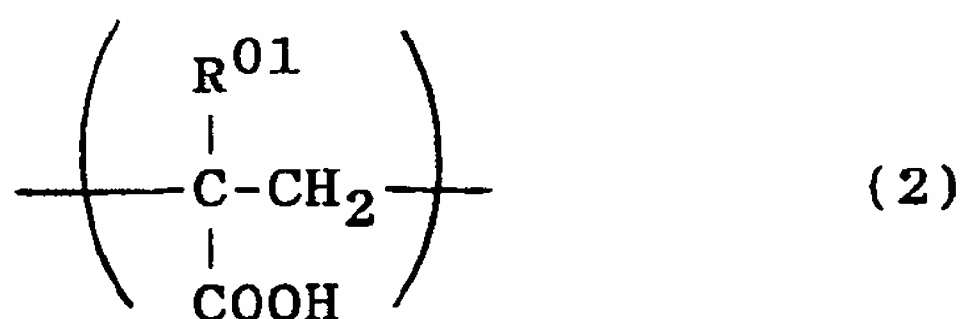
1. A positive resist coating composition comprising:
 - (a) an alkali-soluble resin,
 - (b) at least one radiation-sensitive acid-forming agent selected from the group consisting of an onium salt compound, a halogen-containing compound, a sulfone compound, a nitrobenzyl compound and a sulfonate compound,
 - (c) a compound which has the property of controlling the alkali solubility of the (a) alkalisoluble resin and which is decomposed in the presence of an acid to develop either the property of reducing or losing the effect of controlling the alkali solubility of the (a) alkali-soluble resin or the property of promoting the alkali solubility of the (a) alkali-soluble resin, and
 - (d) at least one solvent selected from methyl 3-methoxypropionate and ethyl 3-ethoxypropionate.
2. The positive resist coating composition of Claim 1, wherein the (a) alkali-soluble resin is a polymer having at least one recurring unit selected from the group consisting of a recurring unit of the formula (1),



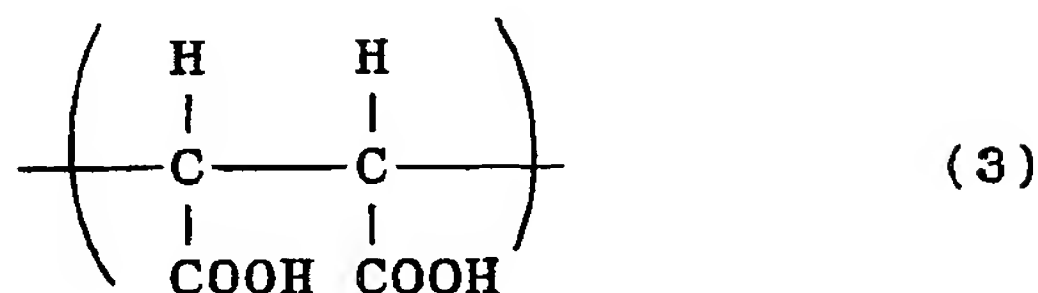
wherein R⁰¹ is hydrogen atom or a methyl group, R⁰² is a hydroxyl group, a carboxyl group, a group of -R⁰³COOH, a group of -OR⁰³COOH or a group of



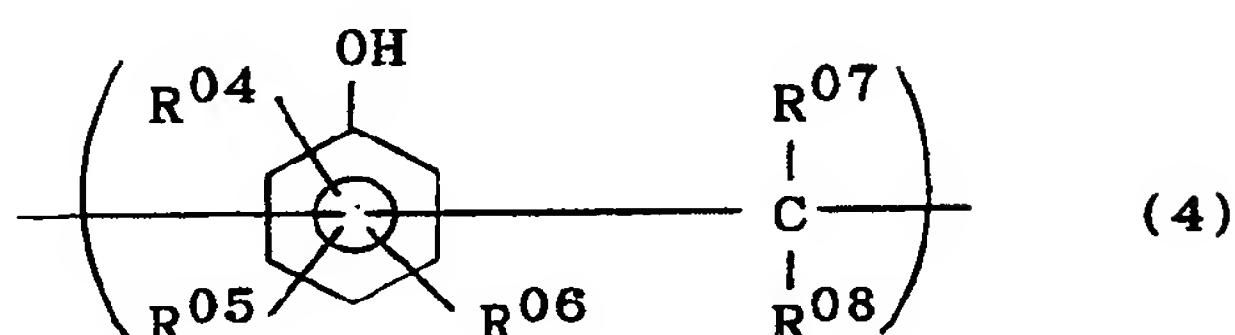
in which R⁰³ is an alkylene group having 1 to 4 carbon atoms, a recurring unit of the formula (2),



wherein R^{01} is as defined in the above formula (1),
a recurring unit of the formula (3),

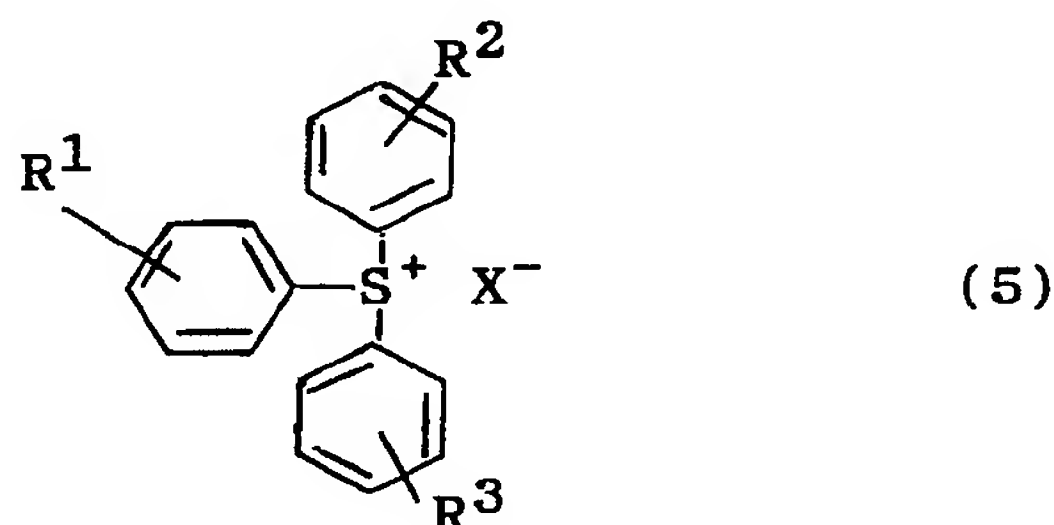


and a recurring unit of the formula (4),

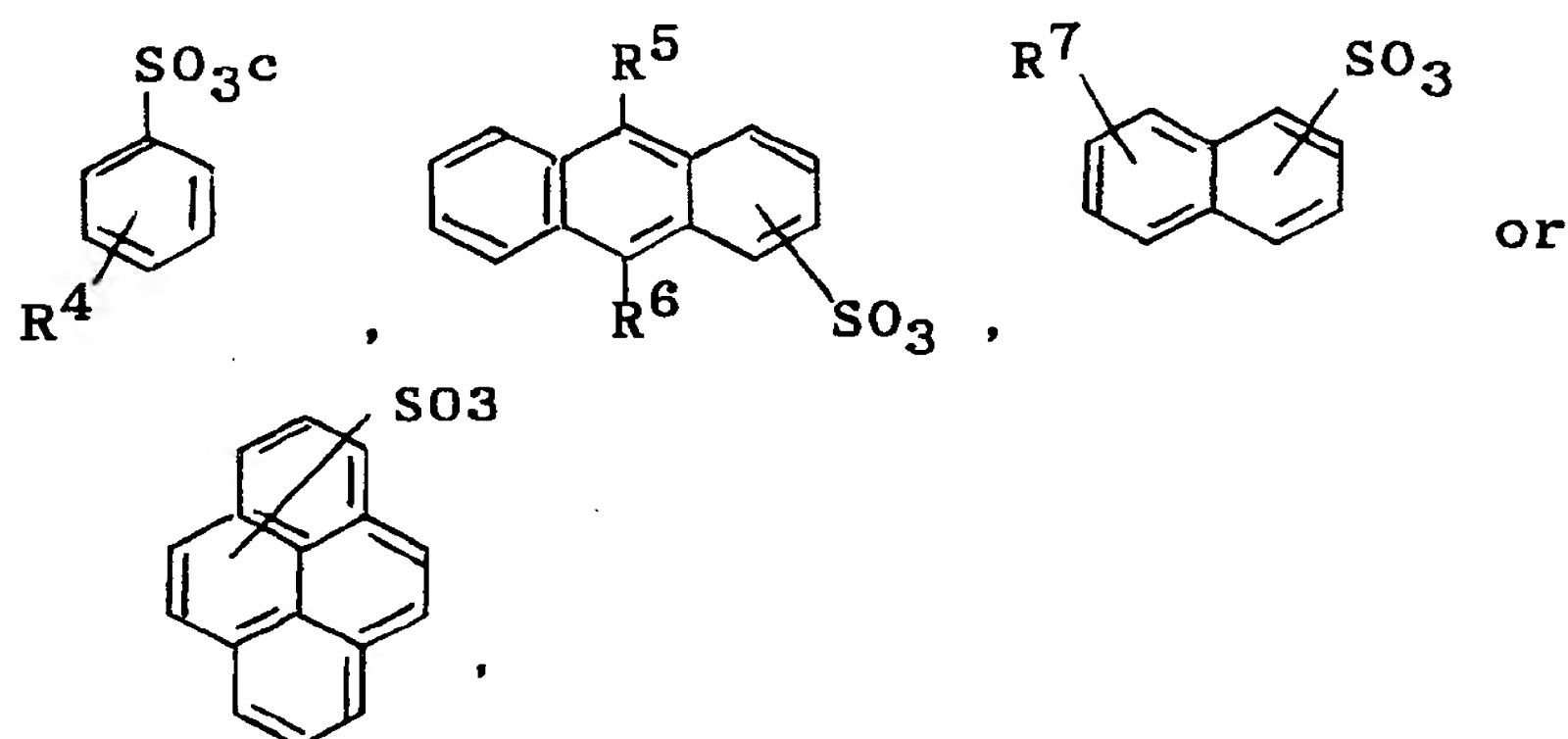


wherein each of R^{04} , R^{05} , R^{06} , R^{07} and R^{08} is independently hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

3. The positive resist coating composition of Claim 1, wherein the (b) radiation-sensitive acid-forming agent is at least one onium salt selected from the group consisting of sulfonium salt of the formula (5),

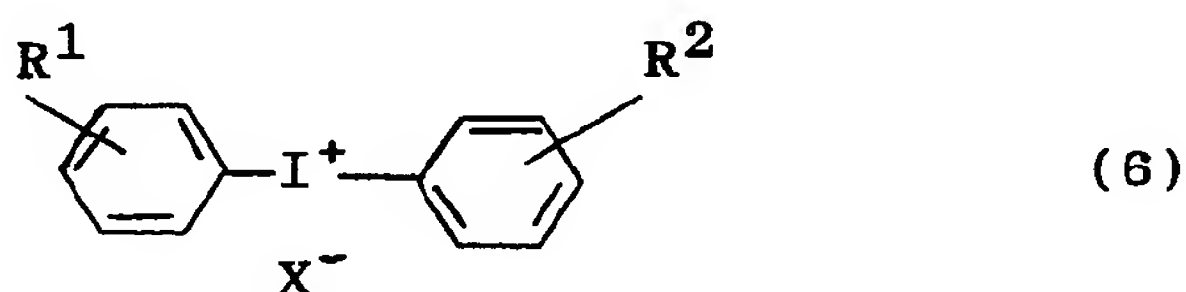


wherein each of R^1 , R^2 and R^3 is independently hydrogen atom, a hydroxyl group, an amino group, a nitro group, a cyano group, an alkyl group having 1 to 4 carbon atoms or an alkoxy group having 1 to 4 carbon atoms, and X is SbF_6 , AsF_6 , PF_6 , BF_4 , CF_3CO_2 , ClO_4 , CF_3SO_3 ,

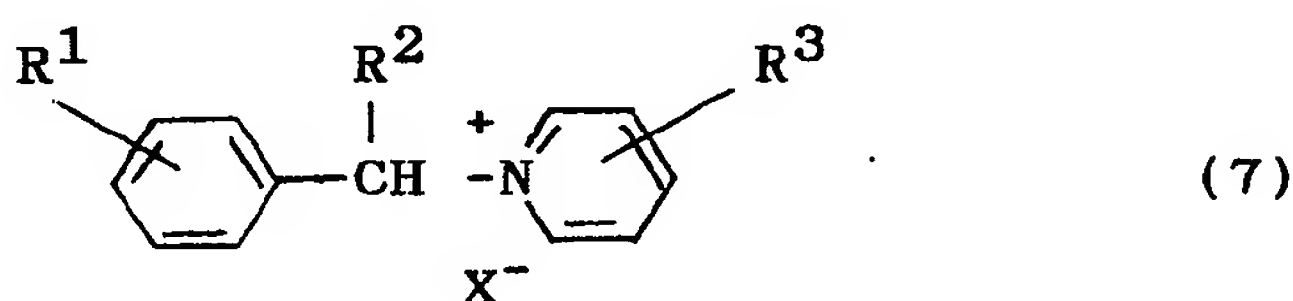


in which R^4 is hydrogen atom, an amino group, an anilino group, an alkyl group having 1 to 4 carbon atoms or an alkoxy group having 1 to 4 carbon atoms, each of R^5 and R^6 is independently an alkoxy group

having 1 to 4 carbon atoms and R⁷ is hydrogen atom, an amino group, an anilino group, an alkyl group having 1 to 4 carbon atoms or an alkoxy group having 1 to 4 carbon atoms, iodonium salt of the formula (6)

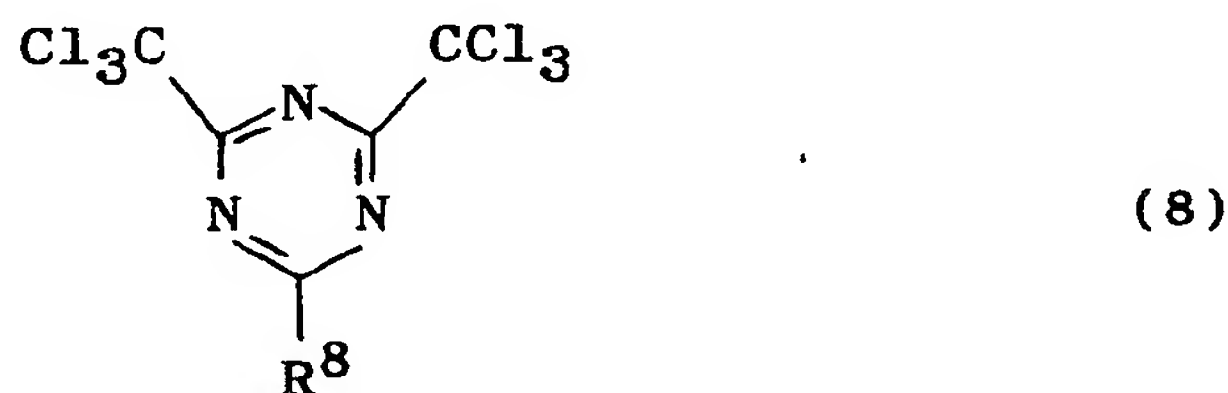


wherein R¹, R² and X are as defined in the above formula (5), and pyridinium salt of the formula (7)

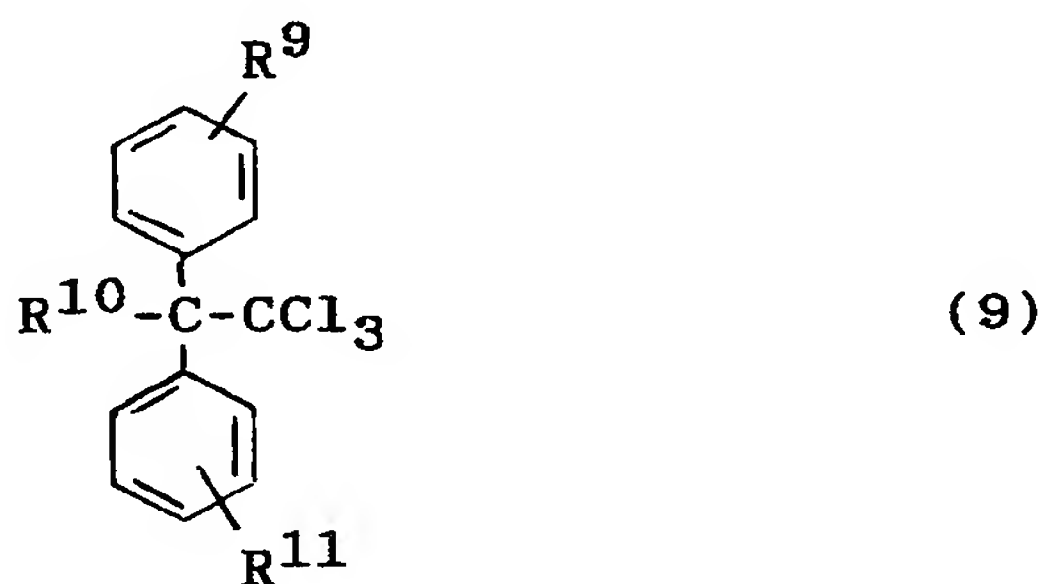


wherein R¹, R², R³ and X are as defined in the above formula (5).

4. The positive resist coating composition of Claim 1, wherein the (b) radiation-sensitive acid-forming agent is at least one halogen-containing compound selected from the group consisting of a compound of the formula (8),

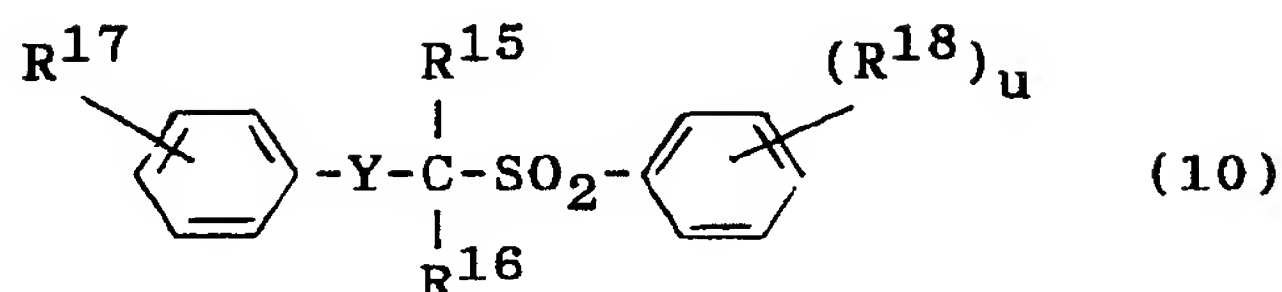


wherein R⁸ is a monovalent organic group, and a compound of the formula (9),



wherein each of R⁹, R¹⁰ and R¹¹ is independently hydrogen atom, a halogen atom, a methyl group, a methoxy group or a hydroxyl group.

5. The positive resist coating composition of Claim 1, wherein the (b) radiation-sensitive acid-forming agent is at least one sulfone compound of the formula (10),

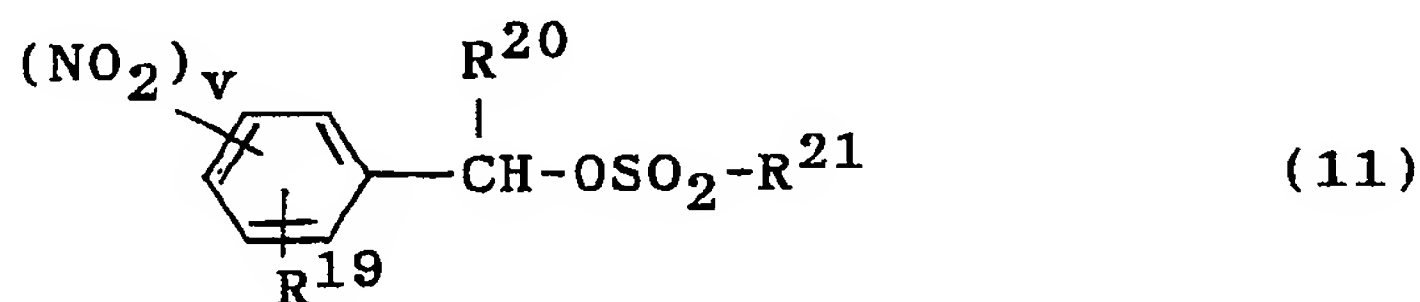


wherein Y is

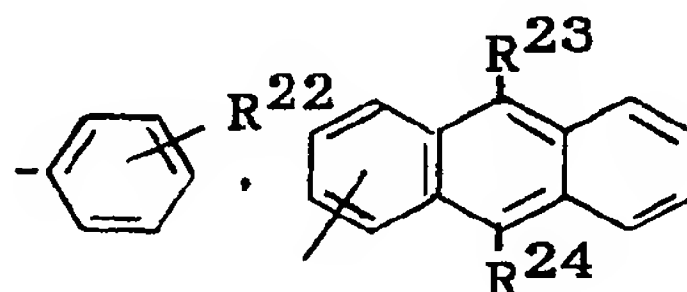


or $-\text{SO}_2-$, each of R^{15} , R^{16} , R^{17} and R^{18} is independently hydrogen atom, an alkyl group having 1 to 4 carbon atoms or a halogen atom, and u is an integer of 0 to 3.

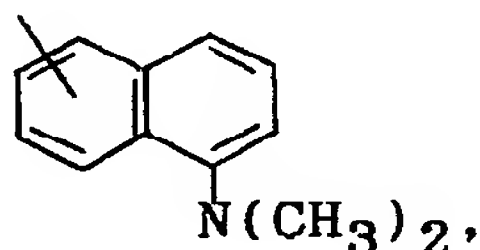
6. The positive resist coating composition of Claim 1, wherein the (b) radiation-sensitive acid-forming agent is at least one nitrobenzyl compound of the formula (11),



wherein R^{19} is an alkyl group having 1 to 4 carbon atoms, R^{20} is hydrogen atom or a methyl group, R^{21} is

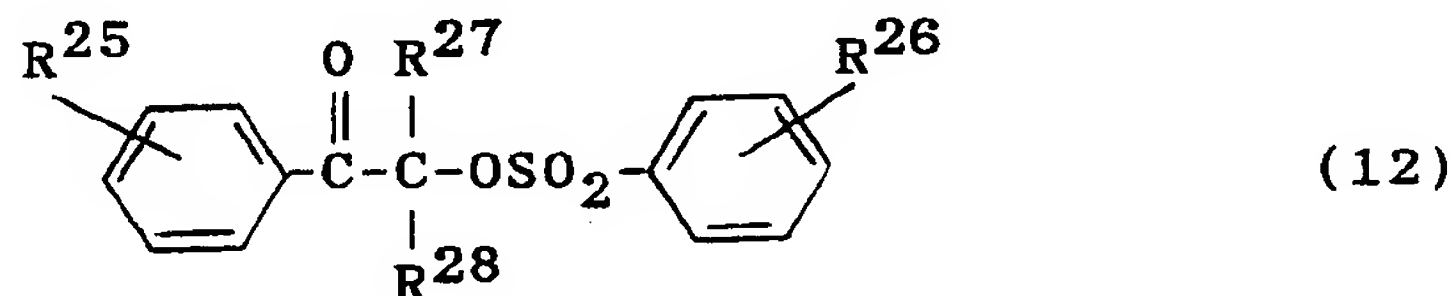


or



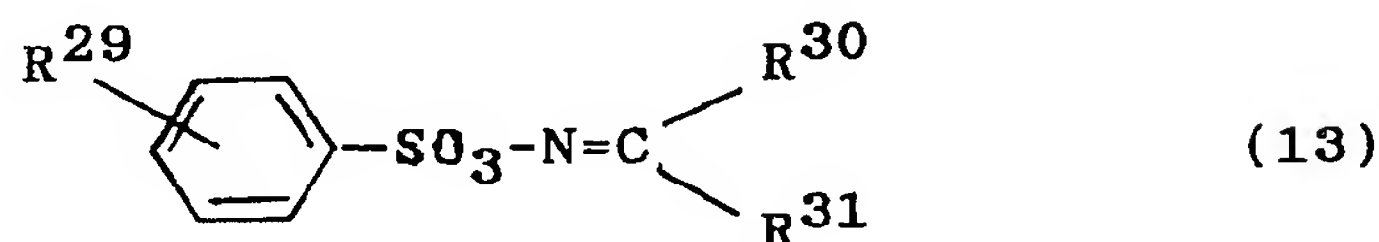
in which R^{22} is hydrogen atom or a methyl group and each of R^{23} and R^{24} is independently an alkoxy group having 1 to 4 carbon atoms, and v is an integer of 1 to 3.

7. The positive resist coating composition of Claim 1, wherein the (b) radiation-sensitive acid-forming agent is at least one sulfonate compound selected from the group consisting of a compound of the formula (12),



wherein each of R^{25} and R^{26} is independently hydrogen atom or an alkyl group having 1 to 4 carbon atoms, each of R^{27} and R^{28} is independently hydrogen atom, an alkyl group having 1 to 4 carbon atoms

or an aryl group having 6 to 20 carbon atoms,
a compound of the formula (13),

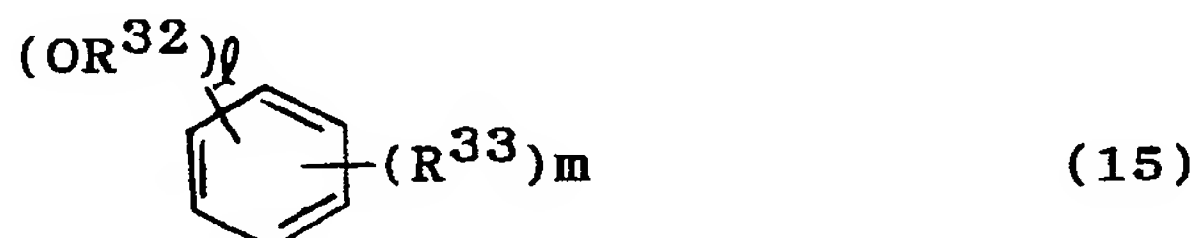


wherein R^{29} is hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and each of R^{30} and R^{31} is independently an alkyl group having 1 to 4 carbon atoms or an aryl group having 6 to 20 carbon atoms, or R^{30} and R^{31} may bond together to form a ring together with a carbon atom to which the R^{30} and R^{31} bond,
and a compound of the formula (14),

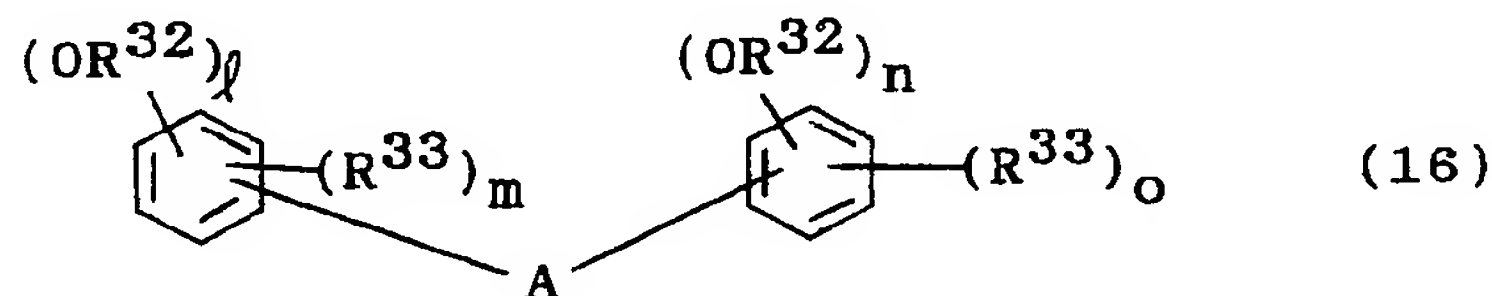


wherein Z is an alkyl group having 1 to 4 carbon atoms, an aryl group having 6 to 20 carbon atoms, trifluoromethyl group or trichloromethyl group.

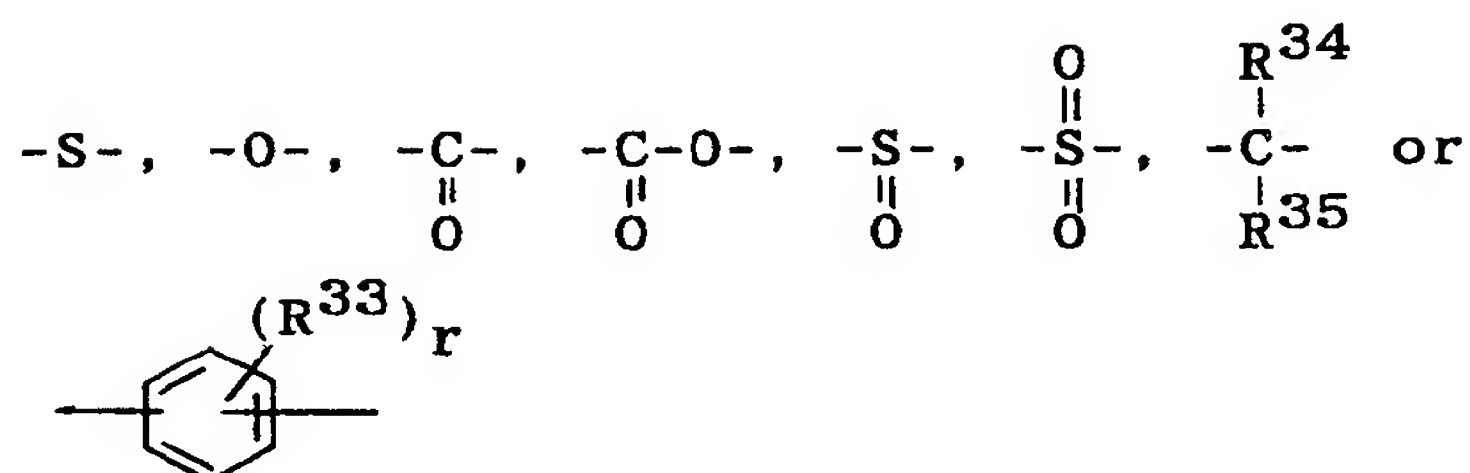
8. The positive resist coating composition of Claim 1, wherein the (b) radiation-sensitive acid-forming agent is contained in an amount of 1 to 70 parts by weight per 100 parts by weight of the (a) alkali-soluble resin.
9. The positive resist coating composition of Claim 1, wherein the (c) compound is selected from the group consisting of at least one compound of the formula (15),



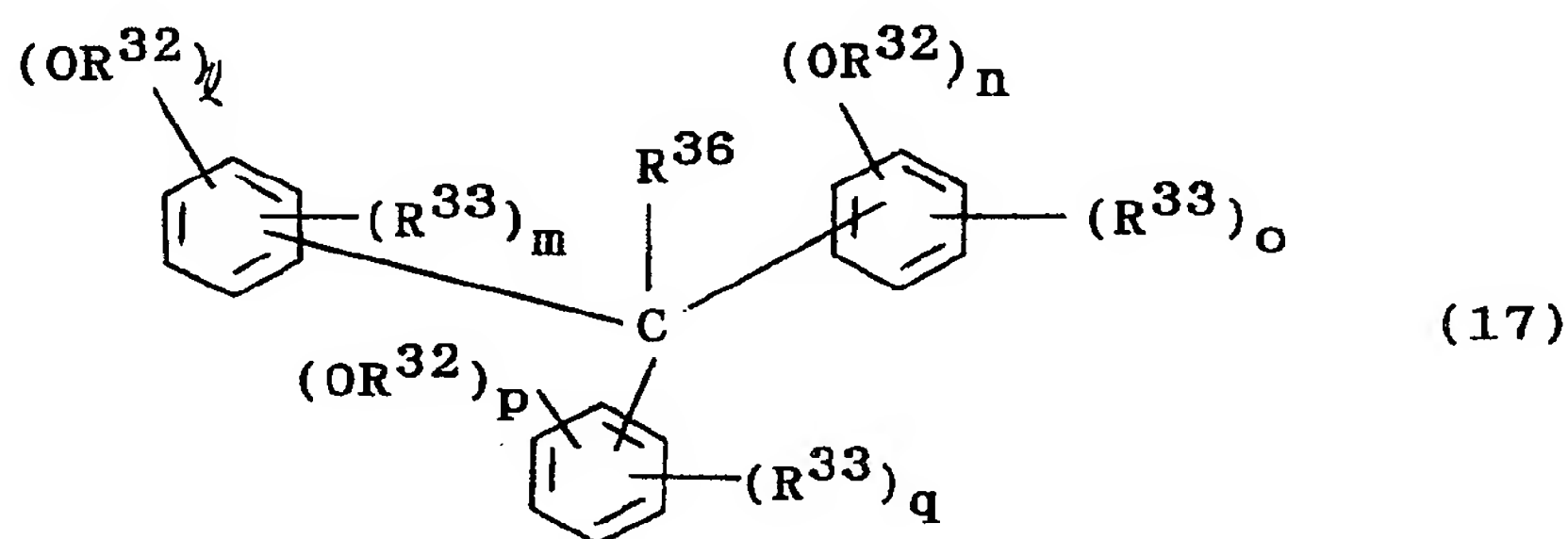
wherein each of R^{32} is independently at least one acid-decomposing group selected from a substituted methyl group, a 1-substituted ethyl group, a germyl group, a silyl group, an alkoxycarbonyl group and an acyl group, each of R^{33} s is independently an alkyl group having 1 to 4 carbon atoms, a phenyl group or a naphthyl group, and ℓ and m are integer of 0 or more which satisfy $\ell+m \leq 6$ and $1 \leq \ell$,
a compound of the formula (16),



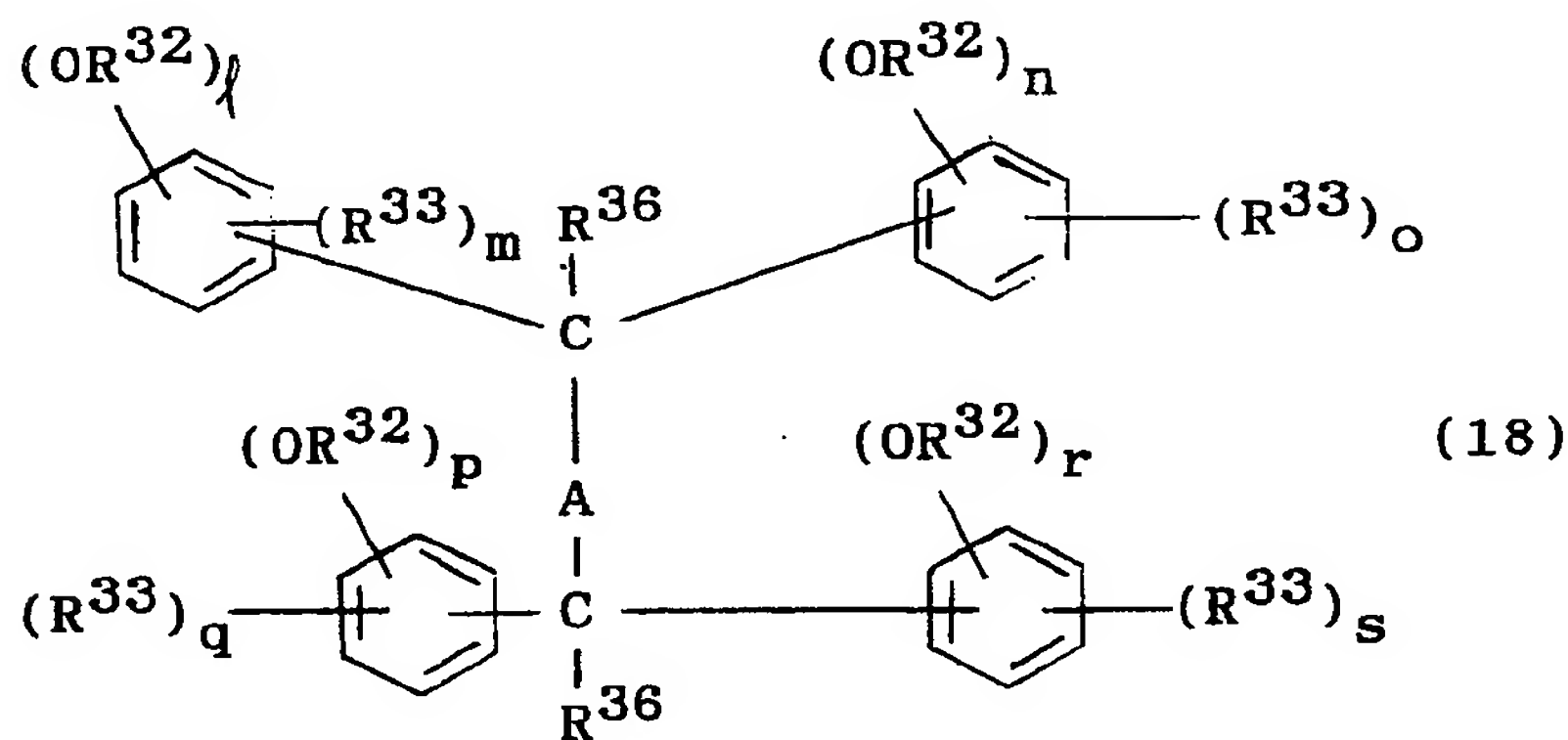
wherein R^{32} and R^{33} are as defined in the above formula (15), ℓ , m , n and o are integers of 0 or more which satisfy $\ell+m \leq 5$, $n+o \leq 5$ and $1 \leq \ell+n$, and A is a single bond,



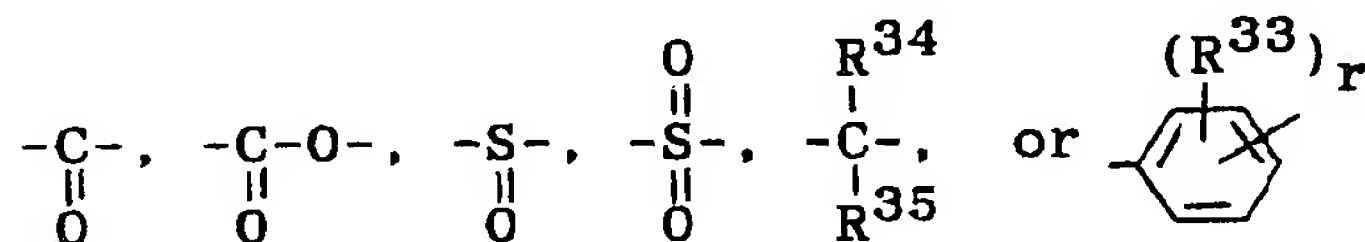
in which R³³ is as defined in the above formula (15) and each of R³⁴ and R³⁵ is independently hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an acyl group, a phenyl group or a naphthyl group and r is an integer satisfying 0 ≤ r ≤ 4,
a compound of the formula (17),



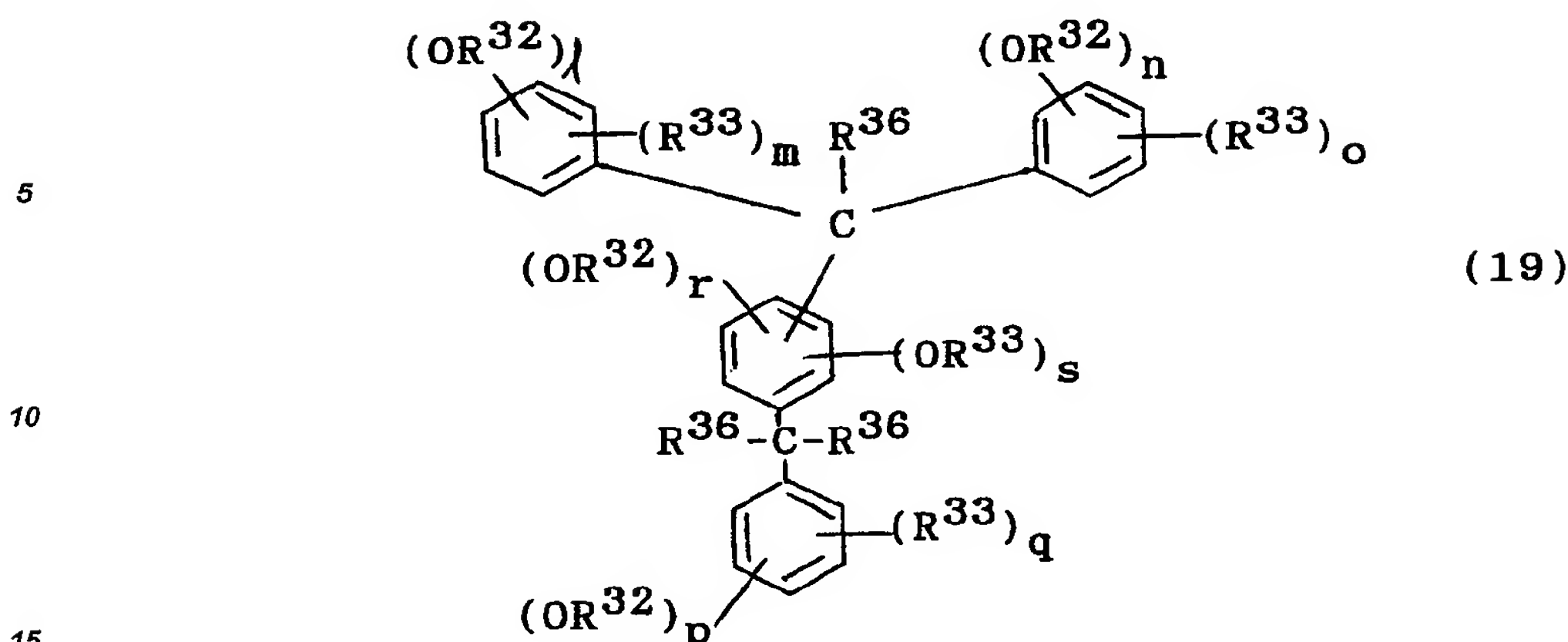
wherein R^{32} and R^{33} are as defined in the above formula (15), ℓ , m , n , o , p and q are integers of 0 or more which satisfy $\ell+m \leq 5$, $o+n \leq 5$, $p+q \leq 5$ and $1 \leq \ell+n+p$, and R^{36} is hydrogen atom, an alkyl group having 1 to 4 carbon atoms or a phenyl group, a compound of the formula (18),



wherein R^{32} , R^{33} and R^{36} are as defined in the above formula (17), ℓ , m , n , o , p , q , r and s are integers of 0 or more which satisfy $\ell+m \leq 5$, $n+o \leq 5$, $p+q \leq 5$, $r+s \leq 5$ and $1 \leq \ell+n+p+r$, and A is a single bond, -S-, -O-,



in which R^{33} , R^{34} , R^{35} and r are as defined in the above formula (16), and a compound of the formula (19),



wherein R^{32} , R^{33} and R^{36} are as defined in the above formula (17), and l , m , n , o , p , q , r and s are integers of 0 or more which satisfy $l+m \leq 5$, $p+q \leq 5$, $n+o \leq 5$, $r+s \leq 4$ and $1 \leq l+n+r+p$.

- 20 10. The positive resist coating composition of Claim 1, wherein the (c) compound is a resin which has at least one acid-decomposing group selected from a substituted methyl group, a 1-substituted ethyl group, a silyl group, a germyl group, an alkoxycarbonyl group and an acyl group and is insoluble or sparingly soluble in an alkali, and which is alkali-soluble when the above group is acid-decomposed.
- 25 11. The positive resist coating composition of Claim 1, wherein the (c) compound is contained in an amount of 5 to 150 parts by weight per 100 parts by weight of the (a) alkali-soluble resin.
- 30 12. The positive resist coating composition of Claim 1, wherein the (d) solvent is contained in an amount of 20 to 3,000 parts by weight per 100 parts by weight of the (a) alkali-soluble resin.
- 35 13. A positive resist coating composition comprising:
 (ac) a resin which has at least one acid-decomposing group selected from a substituted methyl group, a 1-substituted ethyl group, a silyl group, a germyl group, an alkoxycarbonyl group and an acyl group and is insoluble or sparingly soluble in an alkali, and which is alkali-soluble when the above group is acid-decomposed,
 (b) at least one radiation-sensitive acid-forming agent selected from the group consisting of an onium salt compound, a halogen-containing compound, a sulfonate compound, a nitrobenzyl compound and a sulfone compound, and
 (d) at least one solvent selected from methyl 3-methoxypropionate and ethyl 3-ethoxypropionate.
- 40 14. The positive resist coating composition of Claim 13, wherein the (ac) resin is a resin which is obtained by replacing all or part of hydrogen atoms of phenolic hydroxyl group and/or carboxyl group of an alkali-soluble resin (a) with at least one acid-decomposing group selected from a substituted methyl group, a 1-substituted ethyl group, a silyl group, a germyl group, an alkoxycarbonyl group and an acyl group and which is insoluble or sparingly soluble in an alkali.
- 45 15. The positive resist coating composition of Claim 14, wherein the alkali-insoluble or -sparingly soluble resin has the acid-decomposing group in an amount of 15 to 100 mol% of a total amount of the phenolic hydroxyl group and the carboxyl group in the (a) alkali-soluble resin.
- 50 16. A negative resist coating composition comprising:
 (a) an alkali-soluble resin,
 (b) at least one radiation-sensitive acid-forming agent selected from the group consisting of an onium salt compound, a halogen-containing compound, a sulfonate compound, a nitrobenzyl compound and a sulfone compound,
 (c') a compound which crosslinks the (a) alkali-soluble resin in the presence of an acid, and
 (d) at least one solvent selected from methyl 3-methoxypropionate and ethyl 3-ethoxypropionate.
- 55 17. The negative resist coating composition of Claim 16, wherein the (c') compound is an aromatic compound

having a group of the following formula,



wherein each of R^{37} and R^{38} is independently hydrogen atom or an alkyl group having 1 to 4 carbon atoms and R^{39} is hydrogen atom or an alkyl group having 1 to 5 carbon atoms, an aralkyl group having 7 to 20 carbon atoms, a group of $-NR^{40}R^{41}$ in which each of R^{40} and R^{41} is independently an alkyl group having 1 to 4 carbon atoms or a cyclo-ring which has 3 to 8 cyclic member atoms and may contain a hetero-atom, or a group of $-COR^{42}$ in which R^{42} is an alkyl group having 1 to 4 carbon atoms or an aryl group having 6 to 14 carbon atoms,

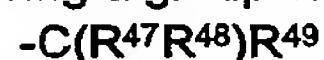
an aromatic compound having a group of the following formula,



wherein R^{43} is hydrogen atom or an alkyl group having 1 to 4 carbon atoms, an aromatic compound having a group of the following formula,



wherein each of R^{44} , R^{45} and R^{46} is independently hydrogen atom or an alkyl group having 1 to 4 carbon atoms, or an aromatic compound having a group of the following formula,



wherein each of R^{47} and R^{48} is independently hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and R^{49} is a three-membered ring which consists of either an oxygen atom or a divalent sulfur atom and of two carbon and hydrogen atoms and which may have a substituent having 1 to 3 carbon atoms.

18. The negative resist coating composition of Claim 16, wherein the (c') compound is contained in an amount of 5 to 95 parts by weight per 100 parts by weight of the (a) alkali-soluble resin.